



## Rapid and Automated Determination of Plutonium and Neptunium in Environmental Samples

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# Rapid and Automated Determination of Plutonium and Neptunium in Environmental Samples

Risø-PhD-Report

Jixin Qiao  
Risø-PhD-75(EN)  
March 2011

Risø DTU  
National Laboratory for Sustainable Energy

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**Title:** Rapid and Automated Determination of Plutonium and Neptunium in Environmental Samples  
**Division:** Radiation Research Division

This thesis is submitted in fulfilment of requirements for the Ph. D. degree at Risø National Laboratory for Sustainable Energy, Technical University of Denmark.

**Abstract:**

This thesis presents improved analytical methods for rapid and automated determination of plutonium and neptunium in environmental samples using sequential injection (SI) based chromatography and inductively coupled plasma mass spectrometry (ICP-MS). The progress of methodology development in this work consists of 5 subjects stated as follows:

- 1) Development and optimization of an SI-anion exchange chromatographic method for rapid determination of plutonium in environmental samples in combination of inductively coupled plasma mass spectrometry detection (**Paper II**);
- (2) Methodology development and optimization for rapid determination of plutonium in environmental samples using SI-extraction chromatography prior to inductively coupled plasma mass spectrometry (**Paper III**);
- (3) Development of an SI-chromatographic method for simultaneous determination of plutonium and neptunium in environmental samples (**Paper IV**);
- (4) Investigation of the suitability and applicability of  $^{242}\text{Pu}$  as a tracer for rapid neptunium determination using anion exchange chromatography in an SI-network coupled with inductively coupled plasma mass spectrometry (**Paper V**);
- (5) Exploration of macro-porous anion exchange chromatography for rapid and simultaneous determination of plutonium and neptunium within an SI system (**Paper VI**).

The results demonstrate that the developed methods in this study are reliable and efficient for accurate assays of trace levels of plutonium and neptunium as demanded in different situations including environmental risk monitoring and assessment, emergency preparedness and surveillance of contaminated areas.

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Thesis for the Degree of Doctor of Philosophy  
Radiation Research Division,  
Risø National Laboratory for Sustainable Energy,  
Technical University of Denmark

# **Rapid and Automated Determination of Plutonium and Neptunium in Environmental Samples**

Jixin Qiao

To be presented with the permission of the Radiation Research Division for public criticism in Risø –  
DTU, Roskilde, Denmark on 17<sup>th</sup> March, 2011.

Roskilde 2011

## Summary in Danish

Denne afhandling præsenterer forbedrede analysemetoder til hurtig og automatisk bestemmelse af plutonium og neptunium i miljøprøver ved brug af sekventiel injektion (SI) baseret på kromatografi og massespektrometri med induktivt koblet plasma (ICP-MS). Metodeudviklingen for dette arbejde er beskrevet i følgende fem artikler.

- 1) Udvikling og optimering af en kromatografisk metode med SI-anionbytter til hurtig bestemmelse af plutonium i miljøprøver kombineret med bestemmelse ved massespektrometri med induktivt koblet plasma (Artikel II);
- 2) Metodeudvikling og optimering til hurtig bestemmelse af plutonium i miljøprøver ved brug af SI-ekstraktionskromatografi og massespektrometri med induktivt koblet plasma (Artikel III);
- 3) Udvikling af en SI-kromatografisk metode til samtidig bestemmelse af plutonium og neptunium i miljøprøver (Artikel IV);
- 4) Undersøgelse af egnethed og anvendelse af  $^{242}\text{Pu}$  som sporstof for hurtig bestemmelse af neptunium med anionbytterkromatografi i et SI-netværk kombineret med massespektrometri med induktivt koblet plasma (Artikel V);
- 5) Undersøgelse af makro-porøs anionbytterkromatografi til hurtig og samtidig bestemmelse af plutonium og neptunium med et SI-system (Artikel VI).

Resultaterne viser, at de udviklede metoder er pålidelige og effektive og giver nøjagtige analyseresultater for spormængder af plutonium og neptunium som krævet i tilfælde af overvågning og vurdering af miljørisici, beredskab og overvågning af forurenede områder.

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## Abstract

This thesis presents improved analytical methods for rapid and automated determination of plutonium and neptunium in environmental samples using sequential injection (SI) based chromatography and inductively coupled plasma mass spectrometry (ICP-MS). The progress of methodology development in this work consists of 5 subjects stated as follows:

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The results demonstrate that the developed methods in this study are reliable and efficient for accurate assays of trace levels of plutonium and neptunium as demanded in different situations including environmental risk monitoring and assessment, emergency preparedness and surveillance of contaminated areas.

## Preface

The present study was carried out at the Radioecology and Tracer Programme, Radiation Research Division, Risø National Laboratory for Sustainable Energy, Technical University of Denmark (DTU), during 2008-2011. I am deeply grateful to Professor Guoan Ye, who was guiding me through the master studies of radiochemistry and offering me the chance to continue my PhD study in Denmark. I am sincerely grateful to Senior Scientist Sven Nielsen who gave me the opportunity to work in his group and advising and encouraging me throughout the whole period of my PhD study.

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## List of publications

This thesis is based on the work contained in the following published papers, which are referred to by their Roman numerals [I-VI].

- I Qiao, J. X., Hou, X. L., Miró, M., Roos, P. Determination of plutonium isotopes in waters and environmental solids: A review. *Analytica Chimica Acta*. 2009, 652, 66-84.
- II Qiao, J. X., Hou, X. L., Roos, P., Miró, M. Rapid Isolation of Plutonium in Environmental Solid Samples Using Sequential Injection Anion Exchange Chromatography Followed by Detection with Inductively Coupled Plasma Mass Spectrometry. *Analytica Chimica Acta*. 2011, 685, 111-119.
- III Qiao, J. X., Hou, X. L., Roos, P., Miró, M. Rapid Determination of plutonium isotopes in environmental samples using sequential injection extraction chromatography and detection by inductively coupled plasma mass spectrometry. *Analytical Chemistry*. 2009, 81, 8185-8192.
- IV Qiao, J. X., Hou, X. L., Roos, P., Miró, M. Rapid and simultaneous determination of neptunium and plutonium isotopes in environmental samples by extraction chromatography using sequential injection analysis and ICP-MS. *Journal of Analytical Atomic Spectrometry*. 2010, 25, 1769-1779.
- V Qiao, J. X., Hou, X. L., Roos, P., Miró, M. Reliable determination of  $^{237}\text{Np}$  using  $^{242}\text{Pu}$  as a potential tracer. *Talanta*. 2011, 84, 494-500.
- VI Qiao, J. X., Hou, X. L., Roos, P., Miró, M. High-throughput Sequential Injection Method for Simultaneous Determination of Plutonium and Neptunium in Environmental Solids Using Macro-porous Anion Exchange Chromatography followed by Inductively Coupled Plasma Mass Spectrometric Detection. *Analytical Chemistry*. 2011, 83, 374-381.

## Abbreviations

AMS	accelerator mass spectrometry
BI	bead injection
EC	electron capture
FI	flow injection
FIA	flow injection analysis
GDMS	glow discharge mass spectrometry
HC	holding coil
HDEHP	bis-2 (ethylhexyl) phosphoric acid
HPLC	high performance liquid chromatography
ICP-MS	inductively coupled plasma mass spectrometry
LOV	lab-on-valve
LSC	liquid scintillation counting
MC-ICP-MS	multicollector inductively coupled plasma mass spectrometry
MDS	multi-solvent delivery system
MPFS	multi-pumping flow system
MS	mass spectrometry
MSFIA	multi-syringe flow injection analysis
Np	neptunium
Pb	lead
Pu	plutonium
RIMS	resonance ionization mass spectrometry
SF-ICP-MS	sector field inductively coupled plasma mass spectrometry
SI	sequential injection
SIA	sequential injection analysis
SIMS	secondary ion mass spectrometry
SNAP	systems for nuclear auxiliary power generator
SP	syringe pump
SV	selection valve
TBP	tri-n-butyl phosphate
Th	thorium
TIMS	thermal ionization mass spectrometry
TOA	trioctylamine-xylene
TOPO	tri-n-octylphosphine
TTA	thenoyl trifluoroacetone
U	uranium

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# 1 Introduction

Plutonium and neptunium, with atomic number of 94 and 93, respectively, are important transuranic elements [1]. Plutonium has 20 isotopes with atomic masses of 228-247, while 19 neptunium isotopes have been characterized in atomic masses from 225 to 244 [2]. The most prevalent isotopes of plutonium and neptunium found in the environment are  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{241}\text{Pu}$  and  $^{237}\text{Np}$  (see Table 1) [2, 3]. Except beta emitting radionuclide  $^{241}\text{Pu}$ , all the others give rise to alpha emission and most of them have long half-lives. Plutonium and neptunium are also readily enriched in the liver and/or bones if introduced into life being. Therefore they are highly hazardous radioactive pollutants in the environment. Although the activity of  $^{237}\text{Np}$  is relatively low in the present environment, however, due to its longer half-life, it will be the prevailing transuranic element in most of nuclear waste after a few hundred years, where most of plutonium and uranium would be removed for further use. Moreover, neptunium is a relatively mobile element in the environment, which makes the diffusion of  $^{237}\text{Np}$  in groundwater a major issue in designing a geological repository for permanent storage of radioactive waste.

As a consequence, the accurate and reliable determination of plutonium and neptunium in environmental samples is important for i) environmental risk assessment and monitoring of the environment around nuclear facilities, such as nuclear power plants, nuclear fuel reprocessing plants and nuclear waste storage sites; ii) emergency preparedness; and iii) surveillance of contaminated areas from nuclear weapon tests, nuclear accidents and discharges of nuclear wastes (see **Paper I**).

Table 1. Nuclear properties of some important neptunium and plutonium isotopes

Radionuclide	$t_{1/2}$	Specific activity (Bq/g)	Principle decay mode	Decay energy (MeV) and intensity (%)
$^{235}\text{Np}$	396.1 d	$5.19 \times 10^{13}$	EC > 99%	-
$^{236}\text{Np}$	154000 yr	$3.64 \times 10^8$	EC 87%	-
$^{237}\text{Np}$	214000 yr	$2.61 \times 10^8$	$\alpha$	$\alpha$ 4.788 (51%), 4.770 (19%)
$^{239}\text{Np}$	2.4 d	$8.42 \times 10^{15}$	$\beta^-$	$\beta^-$ 0.72, $\gamma$ 0.106
$^{238}\text{Pu}$	87.7 yr	$6.34 \times 10^{11}$	$\alpha$	$\alpha$ 5.499 (70.9%), 5.456 (29.0%)
$^{239}\text{Pu}$	24110 yr	$2.30 \times 10^9$	$\alpha$	$\alpha$ 5.157 (70.77%), 5.144 (17.11%)
$^{240}\text{Pu}$	6561 yr	$8.40 \times 10^9$	$\alpha$	$\alpha$ 5.168 (72.8%), 5.124 (27.1%)
$^{241}\text{Pu}$	14.4 yr	$3.83 \times 10^{12}$	$\beta^-$ > 99.99%	$\beta^-$ 0.021
$^{242}\text{Pu}$	375000 yr	$1.46 \times 10^8$	$\alpha$	$\alpha$ 4.902 (76.49%), 4.856 (23.48%)
$^{244}\text{Pu}$	80800000 yr	$6.71 \times 10^5$	$\alpha$ 99.88%	$\alpha$ 4.589 (81%), 4.546 (19%)

## 1.1 Sources of plutonium and neptunium in the environment

Plutonium and neptunium liberated in nuclear weapons testing, particularly in the late 1950s and early 1960s, are by far the largest and global sources of plutonium and neptunium in the environment. The total fallouts have been estimated to be 39 TBq of  $^{237}\text{Np}$ , 330 TBq of  $^{238}\text{Pu}$ , 7.4 PBq of  $^{239}\text{Pu}$ , 5.2 PBq of  $^{240}\text{Pu}$ , 170 PBq of  $^{241}\text{Pu}$  and 16 TBq of  $^{242}\text{Pu}$  [4, 5]. Around 630TBq of  $^{238}\text{Pu}$  was released by the burn-up of the payload in Satellites Systems for Nuclear Auxiliary Power (SNAP) generator in 1964 because of the rocket failure [5-8]. Nuclear reactors and nuclear weapons accidents (e.g. Palomares in 1966; Thule in 1968 and Chernobyl in 1986) [5-8] and discharges from nuclear reprocessing facilities and nuclear power plants are the local sources for plutonium contaminations in the environment (see the details in **Paper I**, Table 2). The local releases of  $^{237}\text{Np}$  are especially arisen

from nuclear reprocessing plant at La Hague and Sellafield, and the Chernobyl accident with estimated inventories of 0.2 GBq, 6.14 TBq and 8 GBq of  $^{237}\text{Np}$ , respectively [9-11].

However, the distribution features of plutonium and neptunium are strongly influenced by the occurrence in different environmental compartments, such as atmosphere, terrestrial environment, aquatic environment, and the concentrations of plutonium and neptunium might vary with the locations. Examples of distribution of plutonium isotopes in some specific oceans and locations related to nuclear accidents are shown in **Paper I**.

## ***1.2 Analytical methods for determination of plutonium and neptunium in environmental samples***

So far, a large number of analytical methods have been developed and exploited for the determination of plutonium and neptunium in various environmental samples, such as soil, sediment, air-borne particulate matter, seawater, groundwater, surface water and wastewater [12-44]. In general, the whole procedure, as presented schematically in Fig. 1, can be divided into four steps: sample pre-treatment, chemical separation and purification, source preparation and detection, wherein chemical separation is the most critical step involving multi-stage operations and determining the analytical reliability and accuracy.

### **1.2.1 Sample pre-treatment**

#### ***1.2.1.1 Preliminary sample treatment***

Preliminary sample treatment normally aims at to decompose the matrix of environmental samples and then extract and/or pre-concentrate the target analytes prior to the chemical separation and purification. For a solid sample, such as soil, sediment, vegetation, tissues and various diets, the sample is firstly ashed in a combustion oven at high temperature (500-800°C) [12-15] to decompose the organic matters. The ashed sample is then normally leached or digested with aggressive acids (e.g., nitric acid, hydrochloric acid and mixture of acids) or totally dissolved with hydrofluoric acid in combination with other acids (e.g., nitric acid, hydrochloric acid and perchloric acid) or with alkali fusion using e.g., hydroxides, peroxides, carbonates, hydrosulfates, pyrosulfates, alkali borates, etc. [16-31] These decomposition methods mentioned above can be performed either with a hot plate or with the assistance of microwave. The application of microwave has the advantages of high efficiency, decreased operational time and amount of reagents, but the sample amount to be pre-treated is limited to a few hundreds of milligrams to a few grams.

In general, acid leaching is the simplest method and suits to the pre-treatment of large amount of sample. However, acid leaching might give rise to poor chemical yields of analyte for samples containing high proportion of refractory oxides of plutonium and neptunium. Plutonium and neptunium hosted in the samples can be completely extracted or dissolved with hydrofluoric acid digestion or alkali fusion, whereupon the losses of target analytes are kept to minimum. Therefore, total dissolution methods are suitable for solid samples containing a large amount refractory plutonium and neptunium. However, increased dissolution of interfering elements, such as uranium, thorium, iron, phosphorus, and rare-earths make the sample pre-treatment somehow cumbersome for analysis of larger sized samples using total dissolution methods, and the working times involved in the manual operation normally restrict the practicability of processing large sized samples, e.g., >5 g of soil or sediment. Moreover, hydrofluoric acid should be removed after dissolution either by fuming with perchloric acid or sulfuric acid or by complexation with boric acid or aluminium in order to facilitate further chemical separations, whereby special extraction facilities for hydrofluoric acid vapours and associated safety

equipment are needed. A drawback of alkaline fusion is the aggressiveness of the reaction that might introduce additional crucible components into the sample matrix.

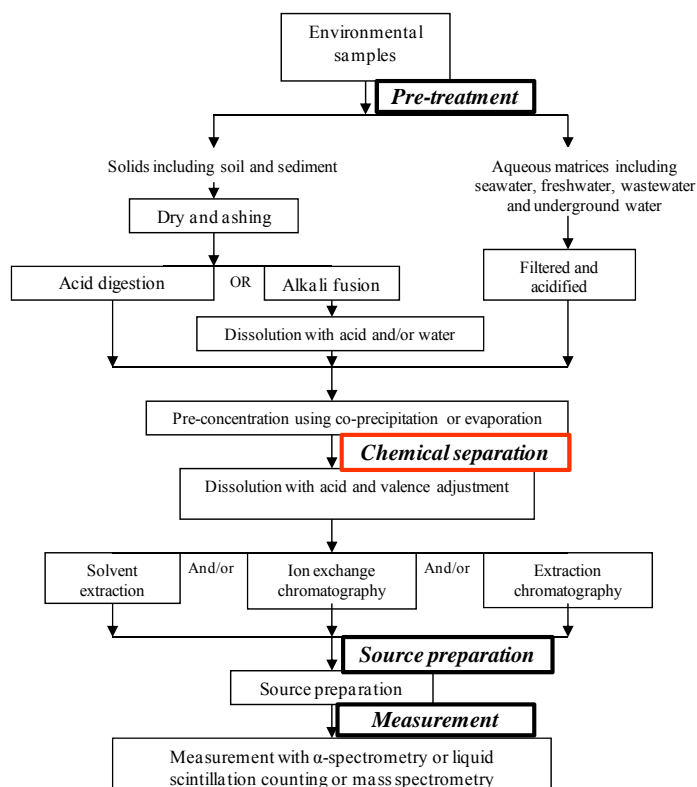


Fig. 1. A general flow sheet for determination of plutonium and neptunium in environmental samples (from **Paper I**)

### 1.2.1.2 Co-precipitation

Co-precipitation is commonly used for the pre-concentration and removal of matrix components in extracts or digests of solid samples following leaching or total dissolution. For aqueous samples, co-precipitation is also mostly exploited following filtration and acidification, except in some cases using evaporation for minute sample with low salt content. The most frequently used co-precipitation reagents for plutonium and neptunium separation are fluorides (e.g.,  $\text{NdF}_3$ ,  $\text{LaF}_3$ ,  $\text{CeF}_3$ ,  $\text{CaF}_2$ ) [16, 24, 32-34],  $\text{Fe}(\text{OH})_2$  and/or  $\text{Fe}(\text{OH})_3$  [13, 19, 31], phosphates ( $\text{CaHPO}_4$ ,  $\text{Ca}_3(\text{PO}_4)_2$ ) [42], and calcium oxalate ( $\text{CaC}_2\text{O}_4$ ) [12].

Co-precipitation of  $\text{Pu}(\text{IV})$  and  $\text{Np}(\text{IV})$  with rare earth fluorides (e.g.,  $\text{NdF}_3$ ) is a commonly used method for preliminary separation of plutonium and neptunium [27, 30] because in this case co-precipitation of  $\text{U}(\text{VI})$  is not favoured, and hereby the interfering effects of uranium are lessened.  $\text{CaF}_2$ -based co-precipitation has also been proven effective for isolation of plutonium and neptunium from soils and sediments [16, 34].  $\text{CaF}_2$  and rare earth fluorides co-precipitations offer another advantage of no risk of precipitation of the main matrix components (e.g. alkali metals and most transition metals) and possible interfering compounds for chemical separation (e.g. phosphate,

sulphate) and/or detection (e.g. U) since the operation is carried out in an acidic media. To be mentioned that in the fluorides co-precipitation methods, plutonium and neptunium have to be converted to Pu(IV) and Np(IV) first, otherwise, the chemical yields of plutonium and neptunium will be reduced, because other oxidation forms of plutonium and neptunium could not form stable water insoluble compounds of fluoride.  $\text{Fe}(\text{OH})_2$  and/or  $\text{Fe}(\text{OH})_3$  are the most commonly used co-precipitation reagents for separation of plutonium and neptunium from leachate of environmental solid samples. They are also selected for isolation of plutonium and neptunium from large volumes of water samples (100-500 L). On the other hand, co-precipitation of plutonium and neptunium with  $\text{CaC}_2\text{O}_4$  is preferred for those samples containing high level of iron, because iron reacts with oxalic acid within the pH range of 5.5-6.0 to form a soluble chelate.

#### **1.2.1.3 Valence adjustment**

Plutonium and neptunium can exist at oxidation states of III, IV, V and VI in environmental samples. The conversion of the overall plutonium and neptunium to a sole oxidation state prior to chemical separation is crucial to ensure high chemical yields of plutonium and neptunium. Since tetravalent plutonium and neptunium in nitric acid medium have the highest retention onto extraction resins and anion exchangers, in most cases, plutonium and neptunium are adjusted to Pu(IV) and Np(IV). To this point, a variety of redox reagents have been used, namely,  $\text{NaNO}_2$  [45],  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{NaNO}_2(\text{s})\text{-HNO}_3$  [19],  $\text{H}_2\text{O}_2\text{-Na}_2\text{S}_2\text{O}_3\text{-NaNO}_2$  [35],  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}\text{-NaNO}_2(\text{s})$  [22],  $\text{NH}_2\text{OH} \cdot \text{HCl}\text{-NaNO}_2(\text{s})$  [13], and  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}\text{-Ascorbic acid}$  [28][46] (see **Paper I** for further information).

#### **1.2.2 Chemical separation**

The accuracy and precision of most analytical methods for plutonium and neptunium are often deteriorated by non-specific interferences resulting from more abundant sample matrix species and spectrometric or isobaric interferences from other nuclides. These interferences often necessitate chemical separation of plutonium and neptunium from the interfering species before detection. Additionally, chemical separations are usually designed to concentrate plutonium and neptunium, which is needed in environmental assays because of the ultra-low levels of target radionuclides. For separation and purification of plutonium and neptunium, a variety of techniques have been used, yet the most common are solvent extraction, ion exchange chromatography, extraction chromatography or a combination of two or more methods [1, 2].

##### **1.2.2.1 Solvent extraction**

Solvent extraction is frequently exploited in the reprocessing of spent nuclear fuel (e.g. PUREX process) and treatment of radioactive waste. Several extraction reagents have been reported for the separation and pre-concentration of plutonium and neptunium including TOA (trioctylamine)-xylene [36, 37], TTA (thenoyltrifluoroacetone)-benzene [43], HDEHP(bis-2(ethylhexyl) phosphoric acid) [41, 44] and TOPO (tri-n-octylphosphine oxide) [38]. In the early days, solvent extraction played an important role for the separation and determination of plutonium and neptunium in environmental samples and now is still used for analysis of highly contaminated samples.

Solvent extraction offers the great advantage of selection among numerous extractants whereby the selectivity can be readily modulated. However, it is deemed too labour-consuming for routine analysis because several extractions should be consecutively performed to completely separate the analyte from the bulk solution. Difficulties in phase separation and the mutual solubility of the two phases might

result in a significant loss of the analyte. Furthermore, a large volume of residual hazardous organic solvents is obtained. Nowadays, because of the development of ion exchange and extraction chromatography, solvent extraction is not often used as a routine method for chemical separation of plutonium and neptunium in environmental samples. Nevertheless, it is flexible and still offers some very attractive features when single samples are analysed. For example, the separation of plutonium using solvent extraction with the combination of tri-n-butyl phosphate (TBP) and TTA, requires less than 1h for complete separation and making the eluate ready for injection to ICP-MS or alpha spectrometry.

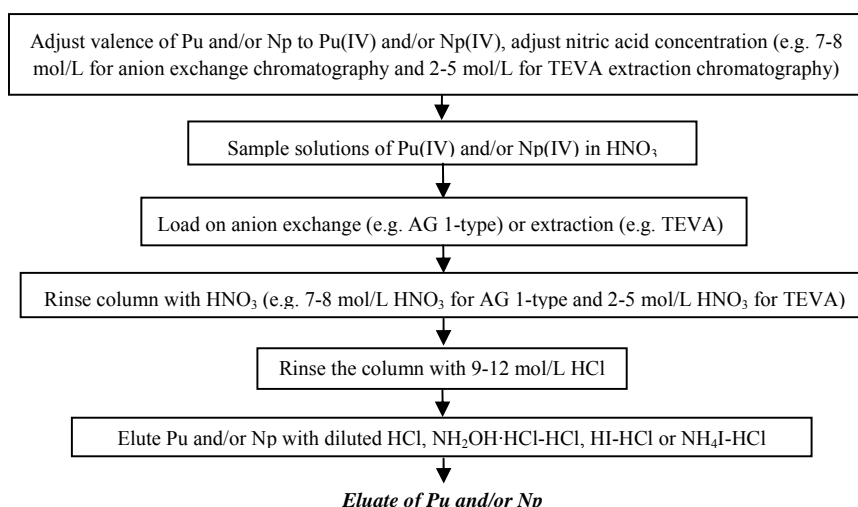


Fig. 2. General flow chart for plutonium and/or neptunium separation using anion exchange or extraction chromatography

### 1.2.2.2 Ion exchange chromatography

Because of the high ionic potential as well as its proclivity to form anionic complexes, plutonium and neptunium might be eventually adsorbed onto either cation or anion exchangers. Ion exchange separation is therefore a common methodology for isolation of plutonium and neptunium in complex matrices. Due to the pronounced ability of actinides to form anionic complexes in the higher oxidation states, anion exchange chromatography using Dowex 1(or AG 1 or AG MP-1M) resins [13, 18, 21, 22, 25, 35, 40], is the most widely accepted method, whereas the cation exchange process is seldom employed [39].

The basis for separation of plutonium and neptunium using anion exchange chromatography relies upon the strong adsorption of anion complexes of Pu(IV) and Np(IV) with NO<sub>3</sub><sup>-</sup> in highly concentrated HNO<sub>3</sub> medium. Most of the matrix elements cannot form anion complexes under this condition, and therefore cannot be retained onto the column. For example, U(VI) only forms a weak anionic complex and thus can be readily separated from Pu(IV) and Np(IV) by rinsing the column with nitric acid. Analytical procedures using anion exchange chromatographic separation for plutonium and neptunium determination generally involve valence adjustment to Pu(IV) and Np(IV), sample loading onto anion exchange column in 7-8 mol L<sup>-1</sup> HNO<sub>3</sub>, rinse the column with 7-8 mol L<sup>-1</sup> HNO<sub>3</sub> to remove most of



inert matrix species, americium and uranium, followed by 9-12 mol L<sup>-1</sup> HCl to remove thorium, and finally elution of plutonium and neptunium using reductant-containing (e.g. TiCl<sub>3</sub>, NH<sub>2</sub>OH·HCl, (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub> or Fe(NH<sub>2</sub>SO<sub>3</sub>)<sub>2</sub>) diluted nitric or hydrochloric acid solutions, or diluted acids forming Pu(IV) and Np(IV) complexes weakly adsorbed onto anion exchangers without changing oxidation states of plutonium and neptunium, e.g., HCl, HF-HNO<sub>3</sub>, HF-HCl or H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>-HNO<sub>3</sub> solution.

Anion exchange chromatography is a classical method that has been given widespread use in most of radio-analytical laboratories for routine analysis of radionuclides in environmental samples. It is cost-effective and provides satisfactory analytical accuracy, selectivity and reproducibility. Nevertheless, in most of reported anion exchange chromatographic methods, large-sized columns (10-20 mL) are exploited to ensure sufficiently high chemical yields of target analytes, whereupon a tedious separation protocol is usually needed consuming a large volume of acidic reagents and consequently generating a considerable amount of waste. However, according to the nominal anion exchange capacity (e.g. 1.0 meq/mL for AG 1-×4), smaller volume (e.g. 2-5 mL) of anion exchange beads might suffice to retain plutonium and neptunium in a moderately high amount of environmental samples (e.g. 10 g of soil). Therefore, from the viewpoint of saving analytical cost, shortening analytical time, and reducing generation of aggressive waste, it is worth to investigate the possibility and applicability of downscaling anion exchange columns for plutonium and neptunium separation.

#### **1.2.2.3 Extraction chromatography**

Extraction chromatography (also called solid phase extraction) is an extraction process performed in a continuous and multi-stage manner on a packed column. In this technique the stationary phase consists of one or more ionophores (extractants), which is immobilized on a porous support material. The inert support is normally composed of porous silica or organic polymers with particle sizes typically ranging between 25-150 μm. Extraction chromatography combines the diversity and selectivity of solvent extraction with the ease of use of a chromatographic column to perform highly efficient separations.

Over the past few years, extraction chromatography has become a very attractive method for plutonium and neptunium separation from environmental samples [28, 31, 32, 34, 36, 42, 47], because of the relatively higher selectivity, shorter separation times, lower consumption of acidic reagents and thus reduced generation of wastes as compared with anion exchange chromatographic methods. The availability of various commercial actinides-specific extraction resins, such as TEVA, TRU, UTEVA and DGA from Eichrom or Triskem, makes plutonium and neptunium extraction chromatographic separations flexible and versatile. However, extraction chromatography is more costly and mostly devoted to scientific research, such as methodology development, therefore less feasible for widespread use in radiochemical laboratories for routine assays.

TEVA and TRU are resins often used for the uptake of plutonium and neptunium in HNO<sub>3</sub> or HCl media [28, 31, 32, 34, 36, 42, 47]. In general, TEVA has better selectivity and decontamination for uranium compared with TRU, because uranium in oxidation state VI is strongly retained by TRU in > 0.5 mol/L of HNO<sub>3</sub>, while weakly bound onto TEVA in diluted HNO<sub>3</sub>. Therefore, in a number of radiochemical procedures, UTEVA has been employed in combination with TRU to improve the separation of uranium from plutonium and neptunium. Another superiority of TEVA over TRU is that simultaneous separation of plutonium and neptunium can be straightforwardly performed by using solely one TEVA column but not in the case of TRU. Th(IV) has similar retention onto TRU as Pu(IV)

and Np(IV) in both HNO<sub>3</sub> and HCl media. Therefore, the elution of plutonium and neptunium cannot be completed simultaneously since on-column reduction of plutonium to Pu(III) and on-column oxidation of neptunium to Np(V) might be involved which cannot be performed at a time.

### **1.2.3 Detection of plutonium and neptunium**

For detection of plutonium and neptunium, either radiometric or mass spectrometric techniques can be employed. In radiometric methods including alpha-spectrometry and liquid scintillation counting (LSC), plutonium and neptunium are measured based on their radioactive decay. In mass spectrometry (MS) including inductively coupled plasma mass spectrometry (ICP-MS) [32, 48], thermal ionization mass spectrometry (TIMS) [49], accelerator mass spectrometry (AMS) [50, 51], resonance ionization mass spectrometry (RIMS) [31], secondary ion mass spectrometry (SIMS) [1], and glow discharge mass spectrometry (GDMS) [1], the atoms of individual plutonium and neptunium isotopes are detected on basis of their respective masses [52].

#### **1.2.3.1 Radiometric method**

##### ***Alpha Spectrometry***

Alpha spectrometry is a technique frequently applied to determine of <sup>238</sup>Pu, <sup>239+240</sup>Pu and <sup>237</sup>Np [2, 4, 53-57]. However, long counting time might be required especially for environmentally levelled radionuclides with low specific activities. In this cases alpha spectrometry may not be well suited for emergency responses. Another problem of importance to safeguards and source identification of plutonium is the overlapping of <sup>239</sup>Pu and <sup>240</sup>Pu peaks when measuring with solid state alpha spectrometry. In addition,  $\alpha$ -spectrometric detection of long-lived <sup>242</sup>Pu and <sup>244</sup>Pu isotopes in environmental samples cannot be accurately performed due to their ultra-trace concentrations and low specific activities.

However, alpha spectrometry, as a traditional radiometric counting method, still plays an important role especially in the detection of plutonium isotopes [12, 18]. Alpha spectrometry is the exclusive technique so far for detection of the relatively short-lived <sup>238</sup>Pu in environmental matrices, which is impossible to be measured by mass spectrometry method because of serious interference from <sup>238</sup>U. In addition, alpha spectrometry has advantages of easy application, relatively low instrumental expenses, robustness and reliability with a near 100% functional up-time. Spectra are simple, thereby minimising the risks of misinterpretation due to potential interfering peaks and presence of stable elements. There is no energy dependent efficiency compared with mass dependent efficiency in mass spectrometry, quantification is simply done by relating to the isotopic yield determination. Detector background can be kept extremely low (e.g., less than 1 count per week in plutonium window) and used for several years without deterioration of background or resolution.

##### ***Liquid Scintillation Counting***

Liquid scintillation counting (LSC) is a generally preferred method of counting weak beta emitters and useful to a lesser extent for alpha and gamma-emitters [54, 58-60]. Because of its poor energy resolution, LSC cannot compete with  $\alpha$ -spectrometry. Nowadays, with the improvement of LSC detectors, the discrimination between <sup>238</sup>Pu and <sup>239+240</sup>Pu is however feasible [61].

LSC has been proved useful for determination of the soft beta-emitter <sup>241</sup>Pu [1]. To this point, the stripping of plutonium out from the source discs is not needed, and therefore these discs can be retrieved again for other purposes after LSC detection. But several problems have been described, e.g.,

whenever some contaminants (e.g. Fe and Pt) are electroplated with plutonium, quenching effects might occur which will decrease the detection efficiency, shift of alpha and beta spectra, and misclassification of alpha/beta events. Furthermore, the LSC results depend on the chemical yields given by alpha spectrometry and the complicated efficiency calibration of the instrument.

### ***Mass Spectrometry***

So far, a vast number of mass spectrometric methods as mentioned above have been introduced to improve the sensitivity and detection limit for determination of plutonium and neptunium in environmental samples as discussed in several review articles [52, 62-65].

### **ICP-MS**

Inductively coupled plasma mass spectrometry (ICP-MS) is a rapidly growing technique and has demonstrated its effectiveness for the measurement of many long-lived radionuclides including plutonium and neptunium at environmental levels. The method has shown a potential application within environmental sciences, including ecosystem tracers and radio-ecological studies, and monitoring of waste discharges. ICP-MS provides much faster answers on the trace concentrations of long-lived radioisotopes, thus avoiding a long counting-time associated with alpha spectrometry.

The simplicity and flexibility of the ICP-MS interface, which allows coupling a variety of multi-solvent delivery systems (MDS), such as, high performance liquid chromatography (HPLC) and flow/sequential injection (FI/SI) system, are attractive features to develop methods that provide significant sample throughput without sacrificing instrumental sensitivity [66-72]. Many protocols have demonstrated the analytical capability of ICP-MS for the on-line determination of specific long-lived radionuclides in a variety of matrices such urine, water, soil, sediment, biological and vegetation and food samples.

Unfortunately, the accurate determination of plutonium and neptunium by ICP-MS is hampered by both spectral and non-spectral interferences. The major problem with spectral interferences is caused by the occurrence of isobars and polyatomic molecules (e.g.,  $^{238}\text{U}$ ,  $^{238}\text{UH}^+$ ,  $^{238}\text{UH}_2^+$  and  $^{241}\text{Am}$ ) as well as tailing of  $^{238}\text{U}$ , which overlap with the measurement of  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{241}\text{Pu}$  and  $^{237}\text{Np}$  isotopes. Thus, ICP-MS detection requires good separation of  $^{238}\text{U}$  prior to determination of plutonium and neptunium.

### **Other mass spectrometric techniques**

Thermal ionization mass spectrometry (TIMS) and accelerator mass spectrometry (AMS), are exceptionally sensitive ion-counting methods that can detect a number of long-lived radionuclides down to the sub-fg range. TIMS with multiple ion collectors was previously the method of choice for isotope ratio measurements with high precision (down to 0.002%), although today multicollector (MC)-ICP-MS has taken this role. TIMS requires an expensive instrument and the separation procedure is so critical that a preliminary sorbent extraction/chromatographic method should be repeated at least twice to separate plutonium and neptunium from matrix constituents. TIMS is also very time consuming, labour intensive and cannot be used for on-line detection because pre-concentration of plutonium and neptunium has to be done manually on a filament. AMS features much lower matrix interfering effects compared with ICP-MS. For plutonium, the main advantage of AMS with respect to conventional MS (TIMS or ICP-MS) is the complete destruction of molecular isobars (e.g.,  $^{238}\text{UH}^+$  for  $^{239}\text{Pu}$ ) by stripping to highly positive charge states in the terminal of the tandem accelerator.

Furthermore the abundance sensitivity is the best among the different mass spectrometry techniques. However, AMS operation is more complex and a well experienced team is required. The scarcity of those instruments and their low sample throughput make them less attractive for emergency response scenarios. Yet, this detection technique is earning popularity because of instrumental developments. Resonance ionization mass spectrometry (RIMS) is well suited for trace analysis of long-lived plutonium and neptunium. RIMS offers a number of assets as compared with other mass spectrometric techniques, including minimization of isobaric interferences, good detection limits, high selectivity and short detection times. However, the application of RIMS is still limited because a limited number of facilities are at disposal. Secondary ion mass spectrometry (SIMS) and glow discharge mass spectrometry (GDMS) are the methods normally used for surface analysis of solid samples, and their detection limits are normally not good enough for analysis of real environmental samples.

### ***1.3 Automated methods for determination of trace-level plutonium and neptunium***

Over the past few decades, a vast amount of effort has been dedicated to the development of accurate and reliable methods for the determination of plutonium and neptunium in various environmental samples. Although the traditional methods developed for plutonium and neptunium chemical separation are sensitive, most of them require tedious chemical separation process and are normally executed in a manual fashion. Therefore they are time-consuming, labor intensive, consequently lower sample throughput and thus not well suited to analyze large number of samples in environmental risk assessment and rapid response in emergency situations. In addition, the long-term contact with aggressive reagents and potentially hazardous samples should be considered as an important risk factor for the analyst.

Flow techniques have no doubt aroused special interest in relation to many automatic methodologies of analysis and have been applied to the determination of many analytes including radionuclides. The combination of classical methods with modern instrumentation makes the full or partial automation of many conventional analytical methods possible in the radiochemical analysis field. This in principle leads to simplicity, reliability, expedite sample processing, significantly decreased labour intensity and improved analyst safety due to the minimum contact with the aggressive acids. Automated methods allow continuous analysis of a number of samples over a long-term working schedule (e.g. overnight or several days) and thus enhance the sample throughput and analytical efficiency. Moreover, with the merit of programmable flow analysis techniques, a precise control of sample and reagent volumes improves reproducibility of analytical methods.

The current flow techniques originates in 1950's, with the segmented flow analysis (SFA) approach. Starting from here, flow analysis has shown an accentuated evolution, especially with the advent of flow injection analysis (FIA), sequential injection analysis (SIA), and recently developed flow techniques including multi-syringe flow injection analysis (MSFIA), lab-on-valve (LOV), bead injection (BI) and multi-pumping flow systems (MPFS) [73-75]. Flow injection (FI)/sequential injection (SI) assemblies have been over the past few years devised for automated analysis of environmental samples contaminated with plutonium and neptunium [76-80]. Fig. 3 graphically illustrates the schemes of a typical FI and SI system. Based on the type of the resins utilized in the separation procedure, FI/SI column separation systems can be divided into two categories, i.e. those involving extraction chromatography and those based on the use of ion exchangers (see **Paper I**).

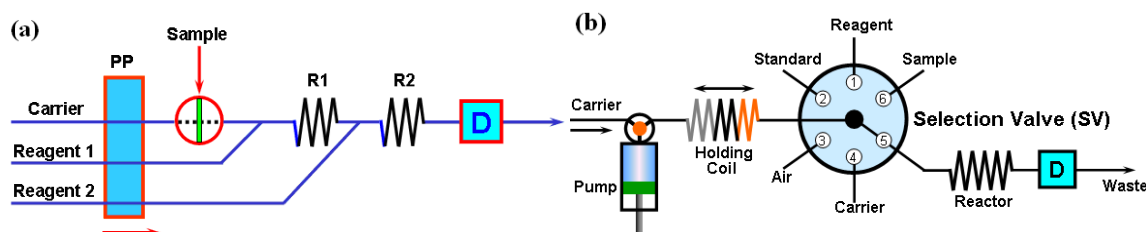


Fig. 3. Diagram of a three-line FI system (a) and an SI set-up furnished with a syringe pump (b)  
PP: peristaltic pump, R1: reaction coil 1, R2: reaction coil 2, D: detector (ref. **Paper I**)

### 1.3.1 FI/SI-based extraction chromatographic separations

The first application of FI/SI for determination of plutonium in artificial samples was reported by Egorov *et al.* [76] in 1998 based on a methodology introduced by Horwitz and co-workers using actinide-specific TRU-resin column [81]. Egorov *et al.* [79] also reported an SI-system for determination of americium, plutonium and neptunium in dissolved vitrified nuclear wastes (in volumes of  $\leq 500\mu\text{L}$ ) using extraction chromatography (TRU) combined with on-line ICP-MS detection. Using the same TRU chromatographic separation procedure, Fajardo *et al.* [77] exploited a multi-syringe flow injection analysis-multi-pumping flow system (MSFIA-MPFS) for automated separation of plutonium and americium for small-sized environmental and biological samples (ca. 1 mL of sample solutions). However, alpha spectrometry was used for quantification of plutonium and americium which makes the measurement somehow time consuming. Truscott *et al.* [78] developed an automated extraction chromatographic method using TRU resin in hyphenation with SF-ICP-MS for determination of plutonium, neptunium, thorium, uranium and americium in reference materials. However, the co-elution of  $^{238}\text{U}$  together with plutonium isotopes in the eluate gave rise to a serious interference at the mass of 239 because of the polyatomic molecule  $^{238}\text{U}^1\text{H}$ , which made this method impossible to determine  $^{239}\text{Pu}$  in sediment. An analytical method for simultaneous determination of  $^{237}\text{Np}$ ,  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  in soils was proposed by Kim *et al.* [80] using an SI system with TEVA-based column separation coupled to SF (sector field)-ICP-MS detection, but it was only applied to  $\leq 4$  g of soil samples. Epov *et al.* [82] reported a rapid on-line analytical method for the determination of plutonium in soils and sediments, in which FI extraction chromatography (TEVA) was exploited to separate and pre-concentrate plutonium from 1 g of soil and sediment samples. An on-line FI separation method for pre-concentration of plutonium and elimination of  $^{238}\text{U}$  with the use of SF-ICP-MS for determination of ultra low level  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  in small amounts ( $\leq 1$  g) of soil and sediment has also been reported [83]. The abovementioned FI-system has also been modified to make it suited for determination of plutonium in 3-10 L of seawater [84].

### 1.3.2 FI/SI-based ion exchange chromatographic separations

Kim and co-workers [70] demonstrated the applicability of flow-through anion-exchange resins (e.g., Dowex 1 $\times$ 8) for the separation and pre-concentration of plutonium in soils. The total time for one-run of separation process was 5.2 h and two samples could be analyzed simultaneously within the designed flow system. Although up to 10 g of soil samples can be processed within the FI system, large-sized anion exchange columns and high consumption of acidic reagents for column separation were required. A protocol for the determination of plutonium in apple leaves (NIST 1515) has been

reported by Epov et al. [85]. Three kinds of resins, i.e., one extraction resin (TRU) and two anion exchange resins (AG 1- $\times$ 8 and AG MP-1M) were investigated and compared with respect to the removal of iron and rare earth elements from plutonium. It was observed that AG MP-1M resin performed better affinity for plutonium compared with TRU and AG 1- $\times$ 8 resins. However, the developed method has only been applied to 10 g of leaf samples spiked with a known amount of plutonium.

On-line coupling of ion-exchange separation with ICP-MS is however not a simple task because of the relatively larger volume of eluent required as compared to extraction chromatography and the incompatibility of common plutonium and neptunium eluents with the detector. Therefore, FI/SI based ion exchange chromatography is frequently performed in an off-line detection fashion, which on the other hand, foster the automated separation of several samples at a time as described in the literature [70].

#### **1.4 Challenges in plutonium and neptunium determination**

Accurate determination of plutonium and neptunium requires the use of appropriate tracers to monitor their chemical yields during chemical separation. Ideally, these tracers should have the same chemical behaviour as the analytes but without occurrence in the sample to be analysed. In the past decades, a number of analytical methods have been developed for the determination of plutonium isotopes in the environment and  $^{236}\text{Pu}$  ( $t_{1/2} = 2.858$  yr),  $^{242}\text{Pu}$  ( $t_{1/2} = 3.75 \times 10^5$  yr) or  $^{244}\text{Pu}$  ( $t_{1/2} = 8.08 \times 10^7$  yr) have been used and performed well as a tracer. However, in the case of  $^{237}\text{Np}$ , no such ideal tracer exists [86, 87]. Although  $^{239}\text{Np}$ ,  $^{236}\text{Np}$  and  $^{235}\text{Np}$  have been used as neptunium isotopic tracers, their limited availability in most laboratories and difficulties in production, purification and/or detection set high demands in the practical operations.

It is in principle possible to perform simultaneous determination of plutonium and neptunium within a single separation procedure because the chemical behaviours of tetravalent plutonium and neptunium anionic complexes are similar in nitric and hydrochloride acid media [1, 88]. Plutonium isotopes, viz.,  $^{242}\text{Pu}$ ,  $^{236}\text{Pu}$  or  $^{244}\text{Pu}$ , might be selected as non-isotopic tracers to monitor the chemical yield of neptunium. The advantage would be the avoidance of difficulties in obtaining isotopic neptunium tracers [89, 90]. Moreover, the analytical time would be shortened because there would be no need for chemical separation of neptunium (*namely*,  $^{237}\text{Np}$ ) from plutonium, and the consumption of samples and chemicals would also be reduced to a large extent. Nevertheless, to the best of our knowledge, only few works have been reported to date for the simultaneous determination of plutonium and neptunium in environmental samples using plutonium as a tracer. Difficulties might arise from the fact that the tetravalent neptunium, being easily oxidized to Np(V), may behave differently from Pu(IV) onto the adsorptive resin during separation.

Over the past few years, attention has been paid to the development of automatic methods involving FI/SI extraction chromatography or anion exchange chromatography for determination of plutonium and neptunium. Most of these methods reported so far were however merely applied to the analysis of highly contaminated samples whereby samples of small size were handled, e.g. soils and sediments of less than 10 g and seawater or effluents (such as nuclear wastewater) of less than 5 L [70, 79, 80, 82-85, 91, 92]. Therefore, they are not suited to separate plutonium and neptunium from large amounts of samples, often tens to hundreds of litres/grams, as required for sensitive quantification of plutonium and neptunium at environmentally relevant levels. In several FI/SI works, the decontamination factors

for matrix elements and interfering radionuclides and the chemical yields of plutonium and neptunium are not stable enough for accurate analysis. The progressive degradation of the sorbent material during repetitive use and sample cross-contamination are other well-known limitations of previously published FI/SI systems with permanent columns.

### ***1.5 Scope of the study***

The objective of the present work is to tackle the above difficulties in order to develop rapid and reliable analytical methods for determination of plutonium and neptunium especially in large-sized environmental samples. This is fulfilled by the following steps:

- i. To investigate an anion exchange chromatographic method for plutonium determination in an SI-network combined with the detection of ICP-MS.
- ii. To investigate SI-extraction chromatography for developing a rapid analytical method for determination of plutonium in environmental samples using ICP-MS detection.
- iii. To investigate SI-based extraction chromatography for simultaneous determination of plutonium and neptunium.
- iv. To investigate the suitability of  $^{242}\text{Pu}$  as a tracer for reliable determination of  $^{237}\text{Np}$  using anion exchange chromatography.
- v. To develop a rapid analytical method for simultaneous determination of plutonium and neptunium in environmental samples.

## 2 Experimental

### 2.1 Instrumentation

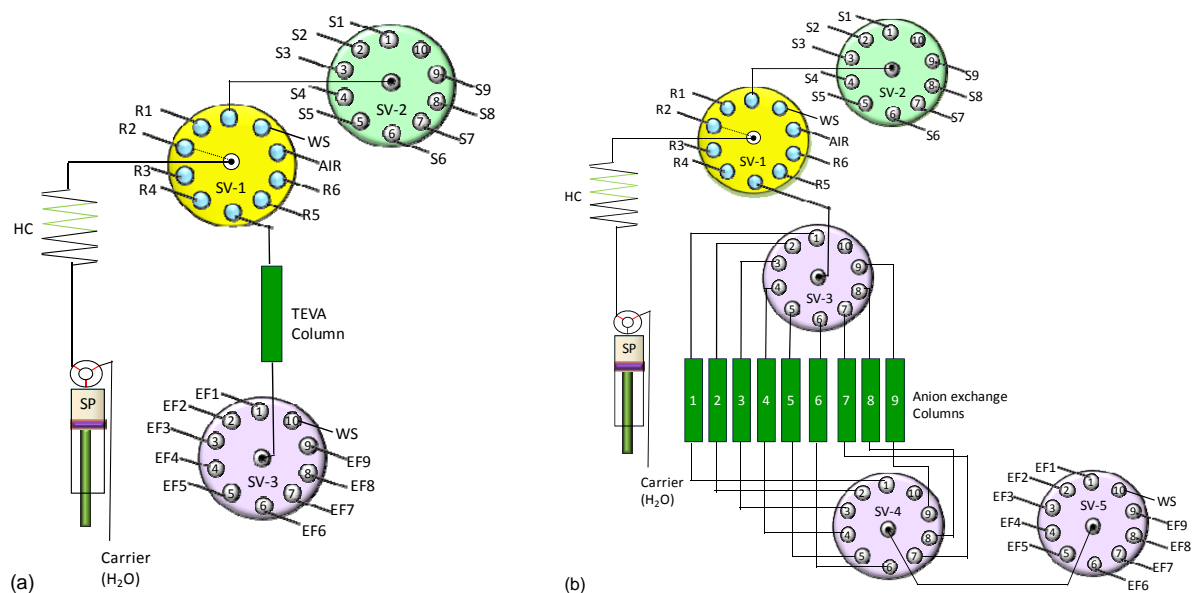


Fig. 4. SI-networks assembled in this study for plutonium and neptunium determination using extraction or anion exchange chromatography ((a) firstly designed SI-analyzer for one sample processing and (b) newly assembled SI-analyzer for nine sample processing). SP: syringe pump, HC: holding coil, S1-S9: ports for sample loading, EF1-EF9: ports for eluate collection, WS: waste, AIR: port for air aspiration to isolation the carrier from the solution drawn into the holding coil, SV-1-SV-5: selective valves, R1-R6: reagents for column separation (details are specified in **paper II-VI**)

The configurations of the SI-manifolds utilized in this study for automated separations of plutonium and/or neptunium consist of an FIALab-3500B SI system (FIALab Instruments, Bellevue, WA) furnished with a syringe pump (SP, Cavo, Sunnyvale, CA, 25 mL capacity), and an internal 10-port (or 6-port) multi-position selection valve (SV-1). The central port of the SV-1 was connected to the holding coil (HC), which consists of a 6.6 m long PTFE tubing with an inner capacity of 30 mL (2.4 mm inner diameter (i.d.)/3.2 mm outer diameter (o.d.)). In the beginning of the design of the SI-system, solely one chromatographic column was incorporated into the SI-manifold and two external 10-port multi-position section valves SV-2 and/or SV-3 (Valco Instruments, Houston, TX) were attached. A schematic illustration of the SI-analyzer is shown in Fig. 4(a). In order to improve the sample processing efficiency and expedite the methodology development, nine separation columns were connected through two external 10-port multi-position section valves, SV-3 and SV-4 (Valco Instruments, Houston, TX) and the schematic illustration of the newly assembled SI-analyzer is given in Fig. 4(b). Other two external 10-port selection valves (SV-2 and SV-5) performed as auto-sampler and eluate auto-collector. Within the system, nine samples can be sequentially processed in a fully automated mode. All the outlets of the selection valve (SV-1) are connected through PEEK ferrules and fittings with rigid PTFE tubing (2.4 mm i.d./3.2 mm o.d.) and all the outlets of the external selection valves (SV2-SV-5) are connected through PEEK ferrules and fittings with rigid PTFE tubing of smaller diameter (0.8 mm i.d./1.6 mm o.d.). The SI-system was fully automatically controlled with the aid of the user-friendly FIALab associated software.



## 2.2 Experimental materials

Solutions of  $^{242}\text{Pu}$  (0.1037 Bq/g in 2 mol/L  $\text{HNO}_3$ ) diluted from NBL-CRM 130 and  $^{243}\text{Am}$  (0.1024 Bq/g in 2 mol/L  $\text{HNO}_3$ ) prepared from NBL-CRM 127 were both purchased from New Brunswick Laboratory (Argonne, IL, USA). A  $^{239}\text{Pu}$  standard solution of 0.100 Bq/g in 2 mol/L  $\text{HNO}_3$  was supplied by Risø National Laboratory for Sustainable Energy (Denmark). Standard solutions of uranium and thorium were purchased from NIST (Gaithersburg, MD, USA). All reagents, including nitric acid ( $\text{HNO}_3$ ), hydrochloride acid ( $\text{HCl}$ ), ammonia ( $\text{NH}_3\cdot\text{H}_2\text{O}$ ), hydroxylammonium chloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ), sodium nitrite ( $\text{NaNO}_2$ ), potassium disulfite ( $\text{K}_2\text{S}_2\text{O}_5$ ), sodium hydroxide ( $\text{NaOH}$ ), ferric chloride ( $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ ), and ascorbic acid used in the experiment were of analytical reagent grade.

TEVA extraction chromatographic resin (25-50  $\mu\text{m}$ , 50-100  $\mu\text{m}$  and 100-150  $\mu\text{m}$  particle size) was purchased from TRISKEM International (Bruz, France). Anion exchange resins explored were of AG 1-type series with different crosslinkage and particle size, including AG 1-  $\times 2$  (2% crosslinked, 50-100 mesh (equal to 297-149  $\mu\text{m}$ )), AG 1-  $\times 4$  (4% crosslinked, 50-100 or 100-200 mesh (equal to 149-74  $\mu\text{m}$ )) and AG 1-  $\times 8$  (8% crosslinked, 50-100 mesh), as well as AG MP-1 M macroporous resins with particle sizes of 50-100 and 100-200 mesh, all resins are in chloride form (Bio-Rad Laboratories Inc., Hercules, CA). The resins were swelled in water and transferred into an Econo-Column® (Bio-Rad Laboratories Inc.) and pre-conditioned with  $\text{HNO}_3$  of identical concentration to the sample loading solution. A number of column sizes with various aspect ratios and inner volume were investigated and compared in this study, including 1.0 cm i.d.  $\times$  20 cm length (ca. 16 mL), 0.7 cm i.d.  $\times$  20 cm length (ca. 8 mL), 0.7 cm i.d.  $\times$  10 cm length (ca. 4 mL), 0.5 cm i.d.  $\times$  10 cm length (ca. 2 mL), 0.7 cm i.d.  $\times$  5 cm length (ca. 2 mL) and 0.5 cm i.d.  $\times$  5 cm length (ca. 1 mL).

Table 2. Summary of samples analyzed in this study

Sample	Sample amount	Description	Sampling area/ location	Relevant paper
IAEA-135 sediment	0.5 or 1 g	Contaminated sediment	Sediment from the Lune Estuary, UK influenced by radioactive discharges from the Sellafield nuclear facility collected in 1991	<b>Papers II-VI</b>
IAEA-385 sediment	1 g	Contaminated sediment	Sediment from the Irish Sea in July 1995	<b>Paper VI</b>
IAEA-375 soil	5 g	Moderately contaminated soil	Obtained from the ‘Staryi Viskov’ collective farm in Novozybkov, Brjansk, Russia in July 1990	<b>Papers II, III</b>
NIST-4359 seaweed	20 g	A blend of <i>Fucus vesiculosus</i> , <i>Laminaria saccharia</i> and <i>Ascophyllum nodosum</i>	Collected from the western coast of Ireland and from the White Sea	<b>Papers II-IV, VI</b>
Irish Sea sediment	0.5 or 1 g	Contaminated sediment	Surface sediment from Irish Sea	<b>Papers II-VI</b>
Danish soil	10 g	Non-contaminated sample ( $<1 \text{ mBq g}^{-1}$ of $^{239}\text{Pu}$ )	Top 10 cm of 2 mm sieved soil from 12 different Danish locations collected in 2003	<b>Papers II-VI</b>
Thule soil	1 g	Contaminated soil	Surface soil from Thule, Greenland	<b>Paper III</b>
Seaweed	20 g	<i>Fucus vesiculosus</i>	Collected from the Klint, Danish coast in the Kattegat in 2003	<b>Papers III, IV, V</b>
Seawater	200 L	Environmental real-life sample	Collected from North Sea in 2008	<b>Paper II</b>
Artificial solution	3 mL	0.1 Bq of $^{242}\text{Pu}$ , 0.1 Bq of $^{243}\text{Am}$ , 0.1 Bq of $^{238}\text{U}$ and 0.04 Bq of $^{232}\text{Th}$ in 3 mL of 3 mol/L $\text{HNO}_3$ solution	Prepared in the lab	<b>Paper III</b>
Artificial solution	15 mL	10 mBq of $^{242}\text{Pu}$ , 1 mBq $^{237}\text{Np}$ and 300 mg of $\text{FeCl}_3$ in 1 mol $\text{L}^{-1}$ $\text{HNO}_3$	Prepared in the lab	<b>Paper IV</b>

Table 2 lists detailed information concerning samples utilized in this study, namely, artificial solutions for investigation of column behaviour of the target radionuclides, reference/certified materials including IAEA-135 sediment, IAEA-385 sediment, IAEA-375 soil and NIST-4359 seaweed and two reference materials from a laboratory round-robin inter-comparison, a Danish soil [93] and an Irish Sea sediment for evaluation of method trueness, as well as real-life samples including seaweed, seawater and Thule soil for method application. Unless otherwise stated, Danish soil was selected for method development.

### 2.3 Sample pre-treatment.

For solid samples including soil, sediment and seaweed, a certain amount of a given sample (0.5-200 g, depending on the concentration of plutonium and neptunium) was placed in a beaker and ashed at 550°C overnight to decompose the organic matters. The ashed sample was spiked with 5-10 mBq of  $^{242}\text{Pu}$  as a chemical yield tracer. For neptunium determination, 0-2 mBq of  $^{237}\text{Np}$  was spiked to some samples to increase the signal of  $^{237}\text{Np}$  in ICP-MS measurement. *Aqua regia* was then added to the sample in a ratio of 10 mL of aqua regia to 1 g of sample, whereupon the mixture was digested on a hotplate at 150°C for 30 min and then 200°C for 2h, respectively. During the digestion, the beaker was covered with a watch-glass to prevent significant evaporation of the solution. After cooling, the supernatant was filtered through a GF/A filter to a centrifuge tube after diluted with some amount of water, the beaker and the filter-paper were washed with 30 mL of 0.2 mol/L HCl. Concentrated ammonia was added to the filtrate to adjust the pH to 8-9, to co-precipitate plutonium and neptunium with iron hydroxides (for seaweed sample, a given amount (ca. 60 mg) of  $\text{FeCl}_3$  was added to the sample before co-precipitation) and to remove most of matrix components. To the co-precipitate obtained after centrifugation, a metered volume (ca. 30 mL) of 6 mol/L NaOH was added to dissolve amphoteric elements, such as aluminium and zinc, and then remove them by centrifugation.

For processing of large size samples, such as 20 g of seaweed and 20-200 g of soil, the sample was initially divided into 2-20 aliquots with a mass of 10 g each to facilitate separation of analytes by co-precipitation. Pre-treatment of the aliquots was preformed simultaneously in a batch-wise approach. After pre-treatment, subsample solutions were combined and subjected to the automated column separation.

For seawater analysis, a certain volume of sample (~ 200 L) was placed in a container and acidified to pH2 with concentrated HCl. To the acidified sample, 10mBq of  $^{242}\text{Pu}$  as a chemical yield tracer, 2g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  as co-precipitation reagent and 100 g of  $\text{K}_2\text{S}_2\text{O}_5$  were added and stirred for 1h to reduce all plutonium to Pu(III). Then, 6 mol/L of NaOH was added to adjust the pH to a value of 10. Pu(III) was co-precipitated with mixed iron and alkaline earth metals hydroxides for  $\geq 5\text{h}$ , and the supernatant was then siphoned off. The slurry was dissolved with concentrated HCl to a final concentration of ca. 0.1 mol/L HCl. 6% (v/v) of  $\text{NH}_3 \cdot \text{H}_2\text{O}$  solution was slowly added to the solution to adjust the pH to 8-9 to co-precipitate plutonium with iron hydroxides for further removal of main matrix constituents such as alkaline earth metals. The resulting precipitate was dissolved in 50mL of concentrated HCl and 50mL of concentrated  $\text{HNO}_3$  in a beaker and the mixture was digested by heat under reflux on a hot-plate (180-200 °C) for 1-2 h. After cooling, the solution was filtered through a GF/A filter, the filtrate was collected into a centrifuge tube and the filter was washed with 30 mL of 0.2 mol/L HCl. Concentrated ammonia was added to the filtrate to adjust the pH 8-9 to co-precipitate the plutonium with iron hydroxides, whereupon the co-precipitate was separated by centrifugation. 30 mL of 6 mol/L of NaOH was added to the precipitate to remove amphoteric elements.

## 2.4 Valence adjustment of Pu(IV) and Np(IV)

Distinct methods for converting overall plutonium and neptunium to Pu(IV) and Np(IV) were investigated and compared in order to optimize the valence adjustment protocol. The detailed experimental conditions can be seen in **Papers II-VI**. Finally, a two-step valence adjustment protocol using the redox pair  $\text{K}_2\text{S}_2\text{O}_5\text{-NaNO}_2$  or  $\text{K}_2\text{S}_2\text{O}_5\text{-HNO}_3$  (highly concentrated) was selected for plutonium and/or neptunium determination and thoroughly investigated.

The procedure for Pu(IV) and Np(IV) valence adjustment can be summarized as follows: a few milliliters of concentrated HCl were added to dissolve the precipitate obtained from the pre-treatment. 200-300 g of  $\text{K}_2\text{S}_2\text{O}_5$  was added to convert the overall plutonium and neptunium to Pu(III) and Np(IV)). 6 mol/L of NaOH was added to the solution to adjust the pH 9-10. For plutonium determination using extraction chromatography (TEVA), the precipitate was dissolved in 1 mol/L  $\text{HNO}_3$  whereupon 100 mg of  $\text{NaNO}_2$  was added to oxidize Pu(III) to Pu(IV). In the other cases of simultaneous determination of plutonium and neptunium using extraction chromatography (TEVA) and plutonium and/or neptunium determination using anion exchange chromatography, concentrated  $\text{HNO}_3$  was added to oxidize Pu(III) to Pu(IV) without change of the oxidation state of Np(IV) and finally the solution was diluted to 8 mol/L  $\text{HNO}_3$  to stabilize Pu(IV) and Np(IV).

## 2.5 Automated separation scheme

The general SI-based on-column separation procedure consists of five steps as follows: I. Rinsing the holding coil and sample inlet and outlet tubing with de-ionized water and/or diluted  $\text{HNO}_3$  at a flow rate of 10 mL/min; II. Pre-conditioning the column with  $\text{HNO}_3$  of identical concentration to the sample loading solution at 2.4 - 3.0 mL/min; III. Loading the sample solution (from 14 to 300 mL, depending on the sample size, e.g., 14 or 15 mL for 10 g of Danish soil) in a 1-8 mol/L  $\text{HNO}_3$  medium (depending on the experimental conditions) onto the column at 1.0-1.2 mL/min to retain the target analytes as anionic nitrate complexes on the column; IV. Rinsing the column with 40-200 mL of 1-8 mol/L  $\text{HNO}_3$  (depending on the experimental conditions) to remove uranium and matrix elements, followed by high concentration of HCl (6 or 9 mol/L, depending on the experimental conditions) to remove thorium; V. Eluting plutonium and/or neptunium with 10-100 mL of 0.1-1.0 mol/L HCl or 0.1 mol/L  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 2 mol/L HCl (depending on the experimental conditions). The flow rates for column rinse and elution of plutonium and/or neptunium varied within method development from 1.0 to 5.0 mL/min and detailed information is presented in **Papers II-VI**.

Aiming at simplification of chromatographic separation and minimization of analyst intervention, nine samples (the maximum number of samples that can be handled with the present system at a given run) were sequentially processed in a fully automated mode within the SI system by assembling nine columns packed with anion exchange resins and altering the experimental conditions (e.g. rinse and elution flow rates and the chemical composition of rinsing solutions and eluents) through the flexible control of the FIALab-associated software. In case of column reuse, 20 mL of 0.1 mol/L  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 2 mol/L HCl followed by 60 mL of 0.1 mol/L HCl or 60 mL of 0.05 mol/L  $\text{H}_2\text{C}_2\text{O}_4$  was exploited for column clean up prior to loading the next sample.

The eluate was evaporated to dryness on a hot-plate to eliminate HCl. 5 mL of concentrated nitric acid was then added and the solution was heated to decompose  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in the case of using 0.1 mol/L  $\text{NH}_2\text{OH}\cdot\text{HCl}$  - 2 mol/L HCl as eluent. The residue was dissolved and reconstituted in 5 mL of 0.5 mol/L  $\text{HNO}_3$  and analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) for

quantification of  $^{237}\text{Np}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{242}\text{Pu}$  and potential interfering nuclides including americium, uranium, thorium, mercury and lead.

## 2.6 Detection of plutonium and neptunium using ICP-MS

To 5 mL of processed sample (diluted in 0.5 mol/L  $\text{HNO}_3$ ), 50  $\mu\text{L}$  of 100  $\mu\text{g/L}$   $\text{In(III)}$  (as  $\text{InCl}_3$ ) was added as internal standard. The concentrations of target analytes (e.g.,  $^{237}\text{Np}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$  and  $^{242}\text{Pu}$ ) and interfering nuclides (e.g.,  $^{238}\text{U}$ ,  $^{232}\text{Th}$ ,  $^{208}\text{Pb}$  and  $^{200}\text{Hg}$ ) were determined using an ICP-MS system (X Series<sup>II</sup>, Thermo Fisher Scientific, Waltham, MA) equipped with an Xs-skimmer cone and a concentric nebuliser under hot plasma conditions. The detection limits calculated as three times of the standard deviation ( $3\sigma$ ) of the processing blank were 1.0 - 1.5  $\text{pg/L}$  for  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{242}\text{Pu}$  and  $^{237}\text{Np}$ . A 0.5 mol/L  $\text{HNO}_3$  solution was used as a washing solution among consecutive assays. No carry-over (memory effect) was observed for consecutive analysis of samples differing in plutonium and neptunium concentrations up to three orders of magnitude. A least-squares regression line was used for quantification of both plutonium and neptunium over the range of 0.01 to 100  $\text{ng/L}$ . From our experimental results, the sensitivity (cps per  $\mu\text{g/L}$ ) of  $^{239}\text{Pu}$  and  $^{242}\text{Pu}$  are identical within 1% uncertainty, which means  $^{242}\text{Pu}$  standard can be used for  $^{239}\text{Pu}$  measurement calibration. Practically, we exploited  $^{242}\text{Pu}$  as a standard for the quantification of  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$  and  $^{242}\text{Pu}$  in the whole study. Prior to detection, the ICP-MS instrument was tuned to maximum transmission of uranium using a 1  $\mu\text{g/L}$  solution of  $^{238}\text{U}$  in 0.5 mol/L  $\text{HNO}_3$  and the instrumental parameters were further adjusted for plutonium and neptunium analyzing 1  $\text{ng/L}$  of  $^{239}\text{Pu}$  and  $^{237}\text{Np}$  solutions to optimal detection efficiency. The typical operational conditions of the instrument are listed in Table 3. It is important to note that these parameters were optimized each time when the instrument was initialized. Typical sensitivities of plutonium (i.e.,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$  and  $^{242}\text{Pu}$ ) and neptunium ( $^{237}\text{Np}$ ) ranged from  $1 \times 10^5$  to  $5 \times 10^5$  cps per  $\mu\text{g/L}$ .

Table 3. Typical operation conditions of ICP-MS for the measurement of plutonium and neptunium

Forward power (W)	1400						
Gas flow rate ( $\text{L min}^{-1}$ )							
Coolant	13.8						
Auxiliary	0.80						
Nebuliser	1.03						
Operation pressures (mbar)							
Expansion	1.5 - 2.5						
Analysis	$5.3 \times 10^{-8}$						
Sample uptake rate ( $\text{mL min}^{-1}$ )	0.3						
Number of replicate runs	3						
Typical $^{238}\text{U}^{1}\text{H}/^{238}\text{U}$ ratio	$5 \times 10^{-5}$						
Typical plutonium sensitivity (cps per $\text{pg g}^{-1}$ )	200-400						
Typical neptunium sensitivity (cps per $\text{pg g}^{-1}$ )	200-400						
Typical processing blank at mass 237, 239, 240 and 242 (cps)	1.0-3.0						
Time resolved data acquisition							
Isotope	$^{208}\text{Pb}$	$^{232}\text{Th}$	$^{238}\text{U}$	$^{237}\text{Np}$	$^{239}\text{Pu}$	$^{240}\text{Pu}$	$^{242}\text{Pu}$
Sweeps	800	800	800	800	800	800	800
Dwell time (ms)	10	10	10	30	30	30	30
Channels per mass	1	1	1	1	1	1	1
Acquisition duration(s)	8	8	8	24	24	24	24

### 3 Results and discussion

In this study, reliable analytical methods were developed for rapid and automated determination of plutonium and neptunium in environmental samples to support different analytical purposes in environmental risk monitoring and assessment, emergency preparedness and surveillance of contaminated areas. Sequential injection anion exchange and extraction chromatographic separations were applied for rapid and automated isolation of target analytes. Inductively coupled plasma mass spectrometric detection was exploited to facilitate expedite quantification. Crucial experimental parameters directing analytical performance of the developed methods involving valence adjustment and maintenance of Pu(IV) and Np(IV), selection of column dimensions and chromatographic resins, removal of interferences, elution of plutonium and neptunium, flow rate, separation capacity, resin reusability, trueness and applicability of the analytical methods and samples throughput are discussed below in detail.

#### 3.1 Valence adjustment and maintenance of Pu(IV) and Np(IV)

Amongst different oxidation states of plutonium and neptunium, TEVA resin and strong basic anion exchangers, such as AG 1 gel type and AG MP-1M macroporous resins, are merely suitable for the adsorption of tetravalent plutonium and neptunium in nitric acid medium, because anionic Pu(IV) and Np(IV) complexes with  $\text{NO}_3^-$  have high retentions onto TEVA and abovementioned anion exchangers [1, 88]. Thus, valence adjustment of overall plutonium and neptunium to Pu(IV) and Np(IV) is crucial to ensure high chemical yields during the separation procedure. Most importantly, in the case of determination of  $^{237}\text{Np}$  using a plutonium isotope as a tracer, the valence adjustment to Pu(IV) and Np(IV) is imperative to ensure the same chemical behaviour of plutonium and neptunium in the chromatographic separation.

Aiming at optimizing valence adjustment conditions for obtaining Pu(IV) and Np(IV), several protocols using different redox reagents including  $\text{K}_2\text{S}_2\text{O}_5$ , ascorbic acid,  $\text{NaNO}_2$ , distinct concentration of  $\text{HNO}_3$  were investigated and compared in this study. Table 4. summarizes the main results in selecting an optimal method for rapid and effective adjustment of Pu(IV) and Np(IV). Our results show that a two-step valence adjustment protocol using the redox pair  $\text{K}_2\text{S}_2\text{O}_5$ - $\text{NaNO}_2$  or  $\text{K}_2\text{S}_2\text{O}_5$ -  $\text{HNO}_3$  (concentrated or 8 mol/L) (see group 1, 4 and 8-10 in Table 4) always performs efficiently for both extraction and anion exchange chromatographic separations, with respect to the reaction time and chemical yields of plutonium and neptunium.

This two-step valence adjustment protocol is based on the reduction of overall plutonium and/or neptunium to Pu(III) and/or Np(IV) with a strong reductant ( $\text{K}_2\text{S}_2\text{O}_5$ ) in acidic condition followed by oxidation of the resulting Pu(III) to Pu(IV) by an moderate oxidant ( $\text{NaNO}_2$  or highly concentrated  $\text{HNO}_3$ ) while maintaining neptunium stabilized as Np(IV). It should be pointed that the effective oxidative reagent in high concentration  $\text{HNO}_3$  solution is actually the same as  $\text{NaNO}_2$ , viz.  $\text{NO}_2^-$ , therefore the principle behind the application of redox pairs  $\text{K}_2\text{S}_2\text{O}_5$ - $\text{NaNO}_2$  and  $\text{K}_2\text{S}_2\text{O}_5$ - $\text{HNO}_3$  (concentrated or 8 mol/L) is identical. The selected two-step valence adjustment is generally fast enough to convert overall plutonium and neptunium into Pu(IV) and Np(IV) in a short time-frame (ca. 30 min). With the merit of co-precipitation performed during the valence adjustment, the sample solution was further purified and thus improved separation efficiency and decontamination of interfering nuclides are expected.

Our investigations on maintenance of Pu(IV) and Np(IV) after valence adjustment demonstrate that highly concentrated (namely 8 mol/L) HNO<sub>3</sub> solution is the optimal milieu to stabilize Pu(IV) and Np(IV). our results show that Pu(IV) and Np(IV) can be stabilized in an 8 mol/L HNO<sub>3</sub> of sample solution for  $\geq 5$  days at 3 °C with equally satisfactory chemical yields of plutonium and neptunium  $\geq 77\%$ . (see **Paper VI**).

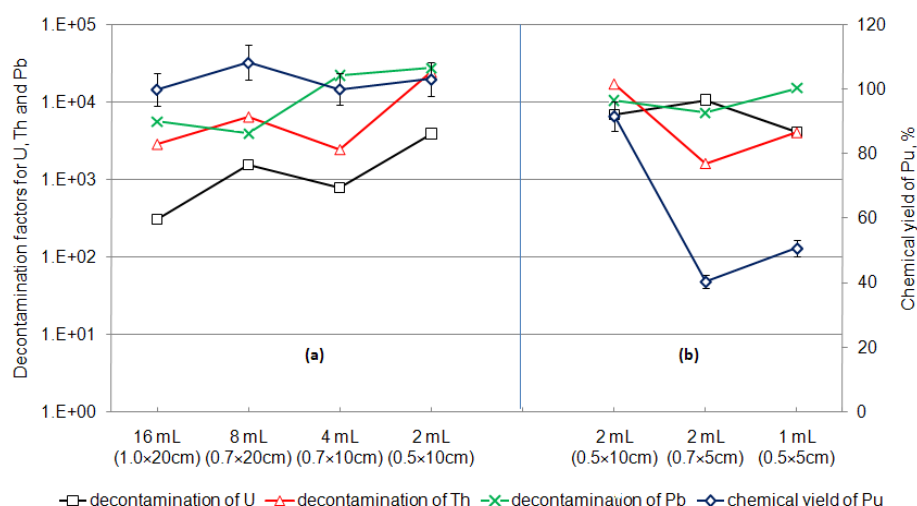


Fig. 5. Effects of column size and dimensions on the chemical yield of plutonium and decontamination factors for uranium, thorium and lead for a) AG 1-4 (50-100 mesh) and b) AG 1-4 (100-200 mesh) resins. (Sample: 10 g of Danish soil. The relative standard deviations for the decontamination factors of uranium, thorium and lead were in all instances better than 10%.) (see **Paper II**)

## 3.2 Optimization of automated chromatographic separations

### 3.2.1 Effect of column size and aspect ratio

The size and aspect ratio of the chromatographic columns are important parameters related to the separation efficiency of plutonium and neptunium from interferences, the chemical yields and the consumption of adsorptive materials and chemicals. In anion exchange chromatographic separations for plutonium and neptunium, traditionally, large volumes of anion exchangers (e.g. 10-20 mL) are often regarded essential for reliable separation [35, 94]. However, this gives rise to relatively large resin and chemical consumption and waste generation. In our study, investigations on separation efficiency of columns with different dimensions were performed in order to downscale anion exchange chromatographic separation for plutonium and neptunium (**in Paper II**). The analytical results (see Fig. 5) reveal that a small-sized ( $\phi 0.5 \times 10$  cm, ca. 2 mL) anion exchange chromatographic columns often suffice for the separation of plutonium and neptunium from  $\geq 10$  g of soil; both 1 mL ( $\phi 0.5 \times 5$  cm) and 2 mL ( $\phi 0.7 \times 5$  cm or  $\phi 0.5 \times 10$  cm) TEVA columns provide satisfactory chemical yields and decontamination factors for interfering nuclides for 10 g of soil samples (**in Paper III**), and the measured concentrations of target analytes agree well with the reference values. By exploiting a small-sized column, remarkable advantages are provided including shortening analytical time, improving analytical capacity, saving analytical cost and reducing generation of aggressive waste.

Table 4. Main valence adjustment protocols for obtaining Pu(IV) and Np(IV)

Group	Redox reagent	Experimental sequence	Target radionuclide	Operation time, min	Separation column	Chemical yield		Relevant paper
						Pu, %	Np, %	
1	K <sub>2</sub> S <sub>2</sub> O <sub>5</sub> -conc. HNO <sub>3</sub> (diluted to 8 mol/L)	Add 300 mg of K <sub>2</sub> S <sub>2</sub> O <sub>5</sub> , stir for 10-20 min. Adjust the pH to 9 with 6mol/L of NaOH, and centrifuge. Dissolve the precipitate with 8 mol/L of HNO <sub>3</sub> .	Pu(IV)	30	AG 1-×4	90.5 ± 3.0	-	<b>Paper II</b>
2	None	-	Pu(IV)	0	TEVA	28.1 ± 7.6	-	<b>Paper III</b>
3	Ascorbic acid	Directly add 300 mg of ascorbic acid to the sample solution in 3 mol/L of HNO <sub>3</sub> and keep the solution for 1 h.	Pu(IV)	60	TEVA	98.5 ± 3.0	-	<b>Paper III</b>
4	K <sub>2</sub> S <sub>2</sub> O <sub>5</sub> -NaNO <sub>2</sub>	Add 300 mg of K <sub>2</sub> S <sub>2</sub> O <sub>5</sub> , stir for 10-20 min. Adjust the pH to 9 with 6mol/L of NaOH, and centrifuge. Dissolve the precipitate with 4 mol/L of HNO <sub>3</sub> , add 100 mg of NaNO <sub>2</sub> and heat for 5 min.	Pu(IV)	40	TEVA	100.0 ± 3.0	-	<b>Paper III</b>
5	K <sub>2</sub> S <sub>2</sub> O <sub>5</sub> -1 mol/L of HNO <sub>3</sub>	Add 200 mg of K <sub>2</sub> S <sub>2</sub> O <sub>5</sub> , stir for 10-20 min. Adjust the pH to 9 with 6mol/L of NaOH, and centrifuge. Dissolve the precipitate with 1 mol/L of HNO <sub>3</sub> .	Pu(IV)&Np(IV)	30	TEVA	3.6 ± 2.8	51.1 ± 7.9	<b>Paper IV</b>
6	K <sub>2</sub> S <sub>2</sub> O <sub>5</sub> -1 mol/L of HNO <sub>3</sub> -ascorbic acid	Add 200 mg of K <sub>2</sub> S <sub>2</sub> O <sub>5</sub> , stir for 10-20 min. Adjust the pH to 9 with 6mol/L of NaOH, and centrifuge. Dissolve the precipitate with 1 mol/L of HNO <sub>3</sub> , add 300 mg of ascorbic acid and wait for 1 h.	Pu(IV)&Np(IV)	90	TEVA	0.2 ± 0.1	43.7 ± 7.7	<b>Paper IV</b>
7	K <sub>2</sub> S <sub>2</sub> O <sub>5</sub> -conc. HNO <sub>3</sub> (diluted to 4 mol/L)	Add 200 mg of K <sub>2</sub> S <sub>2</sub> O <sub>5</sub> , stir for 10-20 min. Adjust the pH to 9 with 6mol/L of NaOH, and centrifuge. Dissolve the precipitate with conc. HNO <sub>3</sub> and then dilute the solution to 4 mol/L of HNO <sub>3</sub> .	Pu(IV)&Np(IV)	30	TEVA	76.7 ± 5.6	73.2 ± 6.1	<b>Paper IV</b>
8	K <sub>2</sub> S <sub>2</sub> O <sub>5</sub> -conc. HNO <sub>3</sub> (diluted to 8 mol/L)	Add 200 mg of K <sub>2</sub> S <sub>2</sub> O <sub>5</sub> , stir for 10-20 min. Adjust the pH to 9 with 6mol/L of NaOH, and centrifuge. Dissolve the precipitate with conc. HNO <sub>3</sub> and then dilute the solution to 8 mol/L of HNO <sub>3</sub> .	Pu(IV)&Np(IV)	30	TEVA	81.8 ± 4.1	80.9 ± 4.0	<b>Paper IV</b>
9	K <sub>2</sub> S <sub>2</sub> O <sub>5</sub> - 8 mol/L of HNO <sub>3</sub>	Add 200 mg of K <sub>2</sub> S <sub>2</sub> O <sub>5</sub> , stir for 10-20 min. Adjust the pH to 9 with 6mol/L of NaOH, and centrifuge. Dissolve the precipitate with 8 mol/L of HNO <sub>3</sub> .	Pu(IV)&Np(IV)	30	TEVA	88.1 ± 3.4	85.7 ± 3.9	<b>Paper IV</b>
10	K <sub>2</sub> S <sub>2</sub> O <sub>5</sub> -conc. HNO <sub>3</sub> (diluted to 8 mol/L)	Add 200 mg of K <sub>2</sub> S <sub>2</sub> O <sub>5</sub> , stir for 10-20 min. Adjust the pH to 9 with 6mol/L of NaOH, and centrifuge. Dissolve the precipitate with conc. HNO <sub>3</sub> and then dilute the solution to 8 mol/L of HNO <sub>3</sub> .	Pu(IV)&Np(IV)	30	AG MP-1M	88.9 ± 4.7	87.2 ± 3.6	<b>Paper VI</b>

Besides column size, the column aspect ratio also affects the separation performance, it was observed in both of extraction and anion exchange chromatographic separations (in **Papers II, IV and V**) that for a ca. 2-mL column, the longer one with smaller diameter ( $\phi 0.5 \times 10$  cm) provided better chemical yields compared with the shorter one with larger diameter ( $\phi 0.7 \times 5$  cm) (see also Fig. 5).

### 3.2.2 Effect of physicochemical properties of resins

Analytical performance was investigated and compared among the three particle sizes of TEVA resin, namely, 25-50  $\mu\text{m}$ , 50-100  $\mu\text{m}$  and 100-150  $\mu\text{m}$  (see **Paper III**). Chemical yields and decontamination factors for uranium, thorium and lead decrease when decreasing the resin particle size, i.e. increasing the specific surface of TEVA particles, for a given volume of rinsing solution. This might be attributed to the varied flow patterns, the differences in functional moieties in the chromatographic column and the presence of the boundary layer with slow exchange rate around the beads of smaller particle grain. Considering the build-up of backpressure within the SI network when packing beads less than 100  $\mu\text{m}$ , the TEVA resin with particle size of 100-150  $\mu\text{m}$  was selected for long-term optimal performance with minimal operational maintenance.

In the anion exchange chromatographic separation of plutonium and/or neptunium, distinct anion exchangers including gel-type resins with different cross-linkage, namely AG 1- $\times$ 2, AG 1- $\times$ 4 and AG 1- $\times$ 8, and macroporous type AG MP-1M resin were tested and compared (see **Paper II, V and VI**). Comparison of the adsorption behaviour between the two particle sizes, viz. 50-100 mesh (corresponding to 297-149  $\mu\text{m}$ ) and 100-200 mesh (or 149-74  $\mu\text{m}$ ), for both AG 1- $\times$ 4 and AG MP-1M resins was also performed (see **Paper II and VI**). Finally, AG 1- $\times$ 4 is regarded as the optimal gel-type anion exchanger for plutonium separation. Smaller particle size is regarded more suitable for samples with higher uranium concentrations due to its relatively higher decontaminations factors for uranium (in **Paper II**).

Interestingly, pre-elution of ca. 30% of neptunium in 9 M HCl rinse step from AG 1- $\times$ 4 resin was observed (see Fig. 6) which induced constantly lowered chemical yields of neptunium compared with plutonium with ratios of  $0.67 \pm 0.04$  ( $n=15$ ) (see **Paper V**). However, better neptunium retention in 9M HCl was obtained for AG MP-1M resin (see **Paper VI**), as a consequence an excellent agreement between the chemical yields of plutonium ( $87.8 \pm 5.0$  %) and neptunium ( $86.8 \pm 6.0$  %) was obtained. This suggests that pore structure, and thus bead permeability plays a remarkable role on the adsorption and elution behaviour of neptunium, and hereby macro-porous AG MP-1M is recommended in the case of simultaneous determination of plutonium and neptunium using a plutonium isotope tracer.

### 3.2.3 Removal of interferences

U, Th, Hg and Pb are naturally abundant elements in most of environmental samples. Large amounts of  $^{238}\text{U}$  and isotopes of Pb prevent accurate quantification of  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$  and  $^{237}\text{Np}$  by ICP-MS, because of isobaric interferences of polyatomic ions  $^{238}\text{U}^1\text{H}$ ,  $^{238}\text{U}^2\text{H}$ ,  $^{208}\text{Pb}^{31}\text{P}$ ,  $^{204}\text{Pb}^{35}\text{Cl}$ ,  $^{206}\text{Pb}^{33}\text{S}$  and tailing of  $^{238}\text{U}$  in 239 and 237 masses region. In addition, high abundance of Th isotopes would induce noisy background in ICP-MS instruments with poor abundance sensitivity due to tailing, which consequently will worsen the detection limits of target analytes and deteriorate the accuracy of the measurement. In order to improve the removal of these potentially interfering nuclides, different washing sequences were investigated and compared in chromatographic separations.



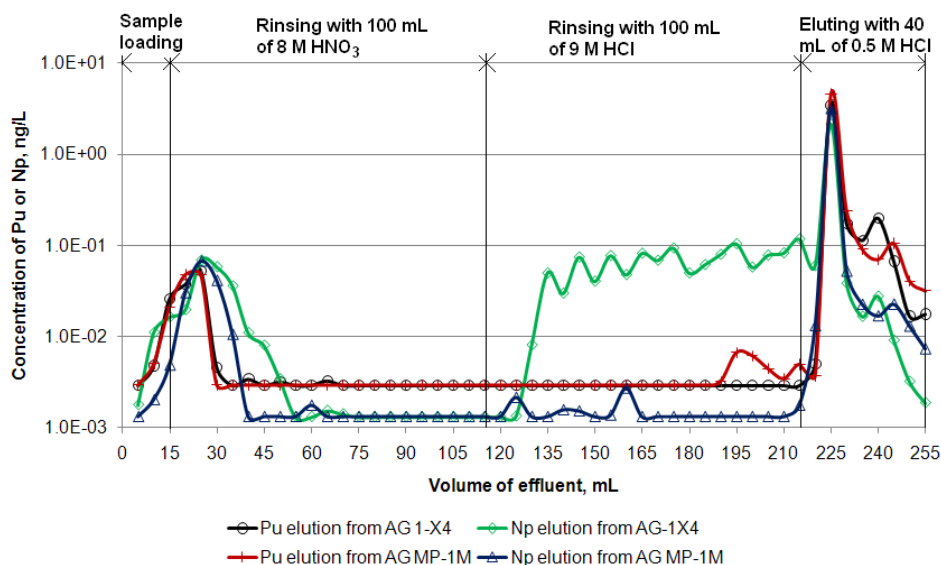


Fig.6 Adsorption and elution behaviour of plutonium and neptunium onto gel-type anion exchanger AG 1- $\times$ 4 (100-200 mesh) and macroporous type resin AG MP-1M (100-200 mesh) (Sample: 10 g of Danish soil, column size: ca. 2 mL ( $0.5 \times 10$  cm), flow rate: 1.2 mL/min)

Nitric acid solutions were always applied for the first column rinsing step to remove most of matrix nuclides and uranium in both extraction and anion chromatographic separations. The results reveal that the larger the volume and the lower the concentration of nitric acid of the rinsing solution, the better are the decontamination factors for uranium. However, lower concentration of nitric acid is not suitable for anion exchange chromatographic separation of plutonium and/or neptunium since chemical yields of plutonium and neptunium dropped dramatically with the decrease in nitric acid concentration (see **Papers II and V**). To ensure high chemical yields of plutonium and neptunium, 8 mol/L  $\text{HNO}_3$  was finally selected as the optimum solution for the first step washing, which is in good agreement with previous works [35].

In the case of plutonium separation with TEVA, high chemical yields ( $> 90\%$ ) always are ensured whenever using nitric acid in a concentration of 1 -3 mol/L, and finally 1 mol/L  $\text{HNO}_3$  was selected as the most effective reagent for the first step column rinsing to obtain the maximum decontamination factors especially for uranium (see **Paper III**). In the case of simultaneous separation of plutonium and neptunium using TEVA column (see **Paper III**), 10 mL of 8 mol  $\text{L}^{-1}$   $\text{HNO}_3$  solution was passed through the column before the 1 mol/L of  $\text{HNO}_3$  rinsing step to stabilize Pu(IV) and Np(IV) and moderately high chemical yields (ca. 60-80%) of plutonium and neptunium were obtained. For the removal of thorium, 6 or 9 mol/L HCl was tested in the second step column rinsing after nitric acid rinsing and finally 9 mol/L of HCl was selected for the removal of thorium throughout this study.

Typical decontamination factors for  $^{238}\text{U}$ ,  $^{232}\text{Th}$ , and  $^{208}\text{Pb}$  using different column separation methods are summarized in Table 5. It can be seen that decontamination factors for thorium differ slightly amongst different methods in the range of  $7.0 \times 10^3$  to  $2.5 \times 10^4$ , while those for lead vary widely from  $1.0 \times 10^3$  to  $1.0 \times 10^5$  due to the external contamination from vessels and reagents. Decontamination factors for uranium are mostly in the range of  $(1-10) \times 10^4$  using TEVA extraction

chromatography, which are 1-2 orders of magnitude higher than those using anion exchange chromatography. This is attributed to the fact that a relatively higher distribution coefficient of uranium (10-20) on anion exchange resins in 8 mol/L of HNO<sub>3</sub> is expected compared with the one (1-2) on TEVA in 1 mol/L of HNO<sub>3</sub>, making uranium not readily to be washed away from the anion exchange column. Nevertheless, according to our calculation, a decontamination factor for uranium of  $2 \times 10^3$  is deemed as the criteria for accurate determination of plutonium and/or neptunium in real-life environmental samples. Under the optimal conditions in anion exchange chromatographic separation, decontamination factors for uranium ranging within  $(3-7) \times 10^3$  were achieved, which basically meets the analytical requirement to obtain reliable analytical results.

### 3.2.4 Elution of plutonium and neptunium from chromatographic columns

For the elution of plutonium from TEVA column, our experimental results (in **Paper III**) indicate distinctly lower decontamination factors for <sup>238</sup>U ( $<10^3$ ) when using 0.1 mol/L NH<sub>2</sub>OH·HCl - 0.1 mol/L HNO<sub>3</sub> as compared with 10-100 fold improved decontamination factors ( $10^4$ - $10^5$ ) when using 0.1 mol/L NH<sub>2</sub>OH·HCl - 2 mol/L HCl. This is most likely a consequence of the low distribution constants of uranium onto TEVA resin in diluted nitric acid solutions, whereby the remaining uranium onto the resin is co-eluted with plutonium.<sup>33</sup> Accordingly, 10 mL of 0.1 mol/L NH<sub>2</sub>OH·HCl-2 mol/L HCl was selected as eluent for plutonium and neptunium from TEVA column (see **Papers III and IV**).

A variety of eluents were investigated and compared for the elution of plutonium from anion exchange columns (in **Paper II**), including HCl solutions in the concentration range of 0.1 to 1.0 mol/L and 0.1 mol/L NH<sub>2</sub>OH·HCl in 2 mol/L HCl. Experimental results for AG 1- $\times$ 4 (100-200 mesh) resin reveal better decontamination factors for uranium and slightly lower decontamination of thorium using diluted HCl as compared with those using 0.1 mol/L NH<sub>2</sub>OH·HCl - 2 mol/L HCl. Finally, 40 mL of 0.5 mol/L HCl was selected as eluent for plutonium and neptunium from all anion exchangers used in this study due to advantages of absence of salts and potential in direct injection of eluate into ICP-MS for on-line measurement of plutonium and neptunium isotopes.

### 3.2.5 Flow rate

Aiming at increasing the sample throughput, and thus improving the analytical efficiency without significantly deteriorating the separation performance, flow rates for column separation within the range of 1.0 to 5.0 mL/min were investigated and compared in this study. At 5.0 mL/min, chemical yields of plutonium and the decontamination factors for interfering nuclides using TEVA resin were still acceptable (see **Paper III**). Nevertheless, because of the increase of the backpressure observed in the SI-column system, the flow rate in the rinsing steps was affixed to 2.5 mL/min for plutonium and neptunium determination using TEVA or gel-type anion exchangers (see **Papers II-V**). The flow rate in the sample loading step was however set to 1.0 mL/min to ensure quantitative uptake of plutonium and neptunium (see **Papers II-V**). For the elution of plutonium and/or neptunium, flow rate was fixed to 1.0 mL/min in extraction chromatographic procedures (in **Papers III and IV**) and 2.5 mL/min whenever using gel-type anion exchangers (in **Papers II and V**). Yet, in the simultaneous separation of plutonium along with neptunium using macro-porous anion exchanger (AG MP-1M) (**Paper VI**), a flow rate above 1.2 mL/min was proven inappropriate, it was observed that the chemical yield ratio of <sup>237</sup>Np/<sup>242</sup>Pu deviated significantly from 1.0. Therefore, flow rates in the overall separation protocol were fixed to 1.2 mL/min when AG MP-1M was used for the simultaneous determination of plutonium and neptunium (see **Paper VI**).

Table 5. Selected analytical results for determination of plutonium and neptunium using SI-based extraction or anion exchange chromatography combined with ICP-MS detection

Method	Analyte	Resin	Chemical yield of $^{242}\text{Pu}$ , $Y_{\text{Pu}}$ (%)	Chemical yield of $^{237}\text{Np}$ , $Y_{\text{Np}}$ (%)	Ratio of $Y_{\text{Np}}/Y_{\text{Pu}}$	$^{239}\text{Pu}$ measured (Bq/kg) *	$^{240}\text{Pu}$ measured (Bg/kg) *	Decontamination factor **		
								$^{238}\text{U}$	$^{232}\text{Th}$	$^{208}\text{Pb}$
Extraction chromatography	Pu	TEVA (2mL, $0.7 \times 5$ cm)	$97.7 \pm 3.4$	-	-	$0.14 \pm 0.01$	$0.09 \pm 0.01$	$7.5 \times 10^4$	$2.5 \times 10^4$	$1.3 \times 10^5$
	Np & Pu	TEVA (2mL, $0.7 \times 5$ cm)	$88.1 \pm 3.4$	$85.7 \pm 3.9$	0.97	$0.14 \pm 0.01$	$0.09 \pm 0.01$	$1.0 \times 10^4$	$7.0 \times 10^3$	$1.0 \times 10^4$
Anion exchange chromatography	Pu (&Np)	AG 1- $\times$ 4 (50-100 mesh), (2mL, $0.5 \times 10$ cm)	$109.5 \pm 8.3$	$75.2 \pm 3.7$	0.69	$0.14 \pm 0.02$	$0.09 \pm 0.01$	$3.9 \times 10^3$	$2.4 \times 10^4$	$2.7 \times 10^4$
		AG 1- $\times$ 4 (50-100 mesh), (2mL, $0.5 \times 10$ cm)	$98.2 \pm 12.0$	$72.8 \pm 4.2$	0.74	$0.14 \pm 0.01$	$0.10 \pm 0.01$	$6.9 \times 10^3$	$1.7 \times 10^4$	$1.0 \times 10^3$
	Np & Pu	AG MP-1M (100-200 mesh), (2mL, $0.5 \times 10$ cm)	$86.5 \pm 4.3$	$85.3 \pm 4.3$	0.99	$0.14 \pm 0.02$	$0.10 \pm 0.01$	$3.9 \times 10^3$	$2.5 \times 10^4$	$1.0 \times 10^4$

\*The sample used in the study is 10 g of Danish soil, the reference values of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  activity concentrations in Danish soil is  $0.140 \pm 0.008$  and  $0.098 \pm 0.006$  Bg/kg, respectively. \*\* The relative standard deviations were in all instances better than 10%.

### **3.3 Recommended SI-separation procedures**

#### **3.3.1 Separation of plutonium**

Since anion exchange chromatography is regarded as classical analytical method for plutonium separation from environmental samples and has an advantage of cost-effective, therefore, in our study, we firstly exploited anion exchange chromatography and optimized the analytical procedure for determination of plutonium in environmental samples (see **Paper II**). Using 10 g of Danish soil as a model sample, the recommended on-column separation procedures using anion exchange chromatography (AG 1- $\times$ 4) is stated below.

#### **Recommended AG 1 - $\times$ 4 procedure for plutonium from 10 g of soil**

- I. Rinse the holding coil with Milli-Q water and sample inlet and outlet tubing with 8 mol/L  $\text{HNO}_3$  at a flow rate of 10 mL/min;
- II. Precondition a ca. 2 mL ( $0.5 \times 10$  cm) column of AG 1- $\times$ 4 (50-100 or 100-200 mesh) anion exchange resin with 8 mol/L  $\text{HNO}_3$  at a flow rate of 3.0 mL/min;
- III. Load the sample solution in 8 mol/L  $\text{HNO}_3$  onto the anion exchange column at a flow rate of 1.0 mL/min;
- IV. Rinse of the column with 100 mL of 8 mol/L  $\text{HNO}_3$  to remove most of the uranium and matrix elements, followed by 100 mL of 9 mol/L HCl to remove thorium at a flow rate of 2.5 mL/min;
- V. Elute plutonium or neptunium with 40 mL of 0.5 mol/L HCl at a flow rate of 2.5 mL/min.

In the developed anion exchange chromatographic protocol, we for the first time downscaled the column size to ca. 2 mL and successfully applied that small-sized column to analyze  $\geq 10$  g of environmental samples. Compared with the earlier works using 10-20 mL of anion exchange column [70, 89], the consumption of resins and reagents for column washing and elution are reduced and thus the separation time is shortened and the generation of acidic waste is minimized. However, a drawback observed in our study using anion exchange chromatography is low decontamination factors especially for uranium which makes the method not very well suited to samples containing high levels of uranium.

Therefore, in our following work, an extraction chromatographic method was developed wherein a small-sized (ca. 2 mL) of TEVA column was exploited. Our analytical results reveal better performance using TEVA column compared with AG 1- $\times$ 4 especially in terms of decontamination of uranium as we mentioned before and the consumption of acidic reagents as well. The optimized TEVA-Pu procedure is summarized as follows for 10 g of soil samples and it is more favourably recommended for plutonium determination especially in environmental samples containing large amounts of uranium.

#### **Recommended TEVA procedure for plutonium from 10 g of soil**

- I. Rinse the holding coil with Milli-Q water and sample inlet and outlet tubing with 1 mol/L  $\text{HNO}_3$  at a flow rate of 10 mL/min;
- II. Precondition a ca. 2 mL ( $0.7 \times 5$  cm) column packed with TEVA (100-150  $\mu\text{m}$ ) resin with 20 mL of 1 mol/L  $\text{HNO}_3$  at a flow rate of 3.0 mL/min;
- III. Load the sample solution in 1 mol/L  $\text{HNO}_3$  onto the extraction chromatographic column at a flow rate of 1.0 mL/min;

- IV. Rinse the column with 60 mL of 1 mol/L  $\text{HNO}_3$  to remove most of the uranium and matrix elements, followed by 60 mL of 9 mol/L  $\text{HCl}$  to remove thorium at a flow rate of 2.5 mL/min;
- V. Elute plutonium with 10 mL of 0.1 mol/L  $\text{NH}_2\text{OH}\cdot\text{HCl}$  - 2 mol/L  $\text{HCl}$  solution at a flow rate of 1.0 mL/min.

### 3.3.2 Simultaneous separation of plutonium and neptunium

Based on the principle that anionic complexes of tetravalent plutonium and neptunium behave similarly on TEVA resin in nitric acid and hydrochloric acid media, we attempted to develop an analytical method for simultaneous determination of plutonium and neptunium using  $^{242}\text{Pu}$  as a chemical yield tracer, and succeed in the method development using TEVA column for simultaneous determination of plutonium and neptunium and obtained a satisfactory performance of  $^{242}\text{Pu}$  as a tracer during the analysis (see **Paper IV**). However, relatively lower chemical yields (60-80%) of plutonium and neptunium were encountered which might be attributed to the low affinity of plutonium and neptunium onto TEVA resin in highly concentrated nitric acid during the first step column rinsing.

Afterwards, we resorted again to anion exchange chromatography due to the higher distribution coefficients of plutonium and neptunium onto anion exchangers in highly concentrated nitric acid and investigated the applicability of  $^{242}\text{Pu}$  as a tracer for neptunium chemical yield monitoring using gel-type anion exchangers (see **Paper V**). The results reveal that AG 1- $\times$ 4 resins could support a reliable determination of neptunium provided under well-defined experimental conditions and the use of a normalization coefficient for calculation of actual chemical yields of  $^{237}\text{Np}$ . However, losses of  $^{237}\text{Np}$  were significant whenever  $^{242}\text{Pu}$  was quantitatively retrieved from the samples, which makes the procedure less attractive. Accordingly, we shifted our strategy to exploit barely used macroporous anion exchangers AG MP-1M, whereby a good agreement between chemical yields of plutonium and neptunium and significantly improved chemical yields of neptunium ( $85 \pm 6\%$ ) using ca. 2 mL of AG MP-1M resin were achieved. We recommend the following analytical procedure using AG MP-1M anion exchanger for simultaneous determination of plutonium and neptunium, which is reliable, efficient and overcoming the difficulties in obtaining a neptunium isotopic tracer in the analysis.

#### Recommended AG MP-1M procedure for plutonium and neptunium from 10 g of soil

- I. Rinse the holding coil with Milli-Q water and sample inlet and outlet tubing with 8 mol/L  $\text{HNO}_3$  at a flow rate of 10 mL/min;
- II. Precondition a ca. 2 mL ( $0.5 \times 10$  cm) column of AG MP-1M (100-200 mesh) anion exchange resin with 8 mol/L  $\text{HNO}_3$  at a flow rate of 2.4 mL/min;
- III. Load the sample solution in 8 mol/L  $\text{HNO}_3$  onto the anion exchange column at a flow rate of 1.2 mL/min;
- IV. Rinse the column with 100 mL of 8 mol/L  $\text{HNO}_3$  to remove most of the uranium and matrix elements, followed by 100 mL of 9 mol/L  $\text{HCl}$  to remove thorium at a flow rate of 1.2 mL/min;
- V. Elute plutonium and neptunium with 40 mL of 0.5 mol/L  $\text{HCl}$  at a flow rate of 1.2 mL/min.

### 3.4 Analytical performance of the proposed SI-based methods

#### 3.4.1 Separation capacity

The developed SI-based methods were evaluated in terms of the reliability for handling large size of sample. To this end, the dependence of the separation efficiency upon the amount of Danish soil processed (from 10 g to 200 g) was investigated. Results presented in Table 6 show the performance of the separation system using ca. 2 mL of TEVA column for up to 200 g soil is satisfactory for accurate determination of low levels of plutonium (see **Paper III**). With a ca. 2 mL of AG 1- $\times$ 4 (50-10 or 100-200 mesh) column, up to 50 g soil can be processed with satisfactory results for plutonium determination. This is the first work where as much as 50 g of environmental solids are handled using a small-sized anion exchange column housed in an SI network (see **Paper II**). In the exploration of ca. 2 mL of AG MP-1M resin for simultaneous separation of plutonium and neptunium, results show that up to 100 g soil sample can be processed with equally satisfactory chemical yields for plutonium (85.2%) and neptunium (79.4%) (see **Paper VI**).

Compared with a reported SI works in which  $\leq 10$  g of soil were processed [70], the proposed analytical methods yield  $\geq 5$  fold better enrichment factors and thus the improvement of minimum detectable concentrations of plutonium and/or neptunium in environmental samples. Moreover, merely one small-sized column sufficed for the entire chemical separation, which makes the SI manifolds more readily compatible and flexible to accommodate multi-stage analytical procedures compared with the two-column associated protocols reported earlier in the literatures [35, 94].

Table 6. Separation capacity of distinct chromatographic methods using a ca. 2 mL of column

Chromatographic Method	Sample size, g	Chemical yield		Ratio of $^{237}\text{Np}/^{242}\text{Pu}$	Measured concentration *, Bq/kg		Ref
		$^{242}\text{Pu}$ , %	$^{237}\text{Np}$ %		$^{239}\text{Pu}$	$^{240}\text{Pu}$	
AG 1- $\times$ 4-Pu	50	70.9 $\pm$ 4.8	-	-	0.14 $\pm$ 0.02	0.11 $\pm$ 0.02	<b>Paper II</b>
	100	34.0 $\pm$ 14.5	-	-	0.13 $\pm$ 0.02	0.10 $\pm$ 0.02	
TEVA-Pu	100	77.0 $\pm$ 12.6	-	-	0.15 $\pm$ 0.03	0.12 $\pm$ 0.03	<b>Paper III</b>
	200	69.3 $\pm$ 22.6	-	-	0.14 $\pm$ 0.01	0.09 $\pm$ 0.02	
AG MP-1M-Pu and Np	50	75.2 $\pm$ 6.3	77.6 $\pm$ 7.2	1.03	0.14 $\pm$ 0.02	0.09 $\pm$ 0.01	<b>Paper VI</b>
	100	85.2 $\pm$ 10.0	79.4 $\pm$ 9.5	0.93	0.14 $\pm$ 0.02	0.10 $\pm$ 0.01	

\*Sample used in this investigation is always Danish soil, the reference values of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  concentrations in this soil were reported to be  $0.140 \pm 0.008$  and  $0.098 \pm 0.006$ , respectively. All values are the average of two replicates ( $\pm$  uncertainty).

#### 3.4.2 Reusability of resins

The potential reusability of the resin is crucial for the development of a fully automated and cost-effective SI-based method for continuous and rapid analysis of a large number of samples. The potential reutilization of the TEVA column as a permanent and integral unit within the SI manifold was investigated using Danish soil as samples (10 g of each) in terms of long-term performance of chemical yields of plutonium, decontamination factors of interferences as well as carryover effects (in **Paper III**). The chemical yields of plutonium for the first twenty samples were within the range of 95%-105% and negligible ( $<0.1\%$ ) carryover was observed, which indicates the feasibility of implementation of a reusable TEVA column in the flow network for continuous sample analyses. Actually, our experimental results showed that the chromatographic column could be reused for up to about forty

times, but after 20 runs, an increased flow backpressure was eventually observed. Notwithstanding the fact that decontamination factors for  $^{238}\text{U}$ ,  $^{232}\text{Th}$  and  $^{208}\text{Pb}$  decreased slightly with the reutilization of the resin, average values of  $6.9 \times 10^4$ ,  $1.6 \times 10^4$  and  $2.0 \times 10^4$  were obtained for  $^{238}\text{U}$ ,  $^{232}\text{Th}$  and  $^{208}\text{Pb}$ , respectively, which suffice for accurate determination of plutonium in environmental samples.

The reusability of AG MP-1M column was also evaluated by handling 10 g of Danish soil spiked with different amounts of  $^{237}\text{Np}$ , the results indicates that a ca. 2 mL column packed with AG MP-1M resin could be reused for up to 10 times with satisfactory chemical yields (> 70%). However, subtle deviations of measured  $^{237}\text{Np}$  and plutonium isotopes values from the expected concentrations were noted in some instances (see **Paper VI**). This might be a consequence of the incomplete removal of plutonium and neptunium from the anion exchanger with the usage of 60 mL of 0.05 mol/L  $\text{H}_2\text{C}_2\text{O}_4$  for column clean-up between samples. Maximum analyte carry-over of 5% for  $^{242}\text{Pu}$  and 0.5% for  $^{237}\text{Np}$  was detected in the consecutive processing of two Danish soil samples spiked with ca. 20 mBq of  $^{242}\text{Pu}$  and ca. 2 mBq of  $^{237}\text{Np}$ . Therefore, attention should be paid when reusing the AG MP-1M resin for processing a variety of samples with different concentration levels of analytes, wherein stronger clean-up chemicals, e.g., HF or EDTA might be needed to minimize carry-over effects.

### 3.4.3 Trueness and applicability of the analytical methods

To assess the trueness and applicability of the proposed analytical methods for handling environmental samples with different levels of plutonium and neptunium and of variable matrix complexity, standard reference materials and some real samples were analyzed after method development and optimization (see **Papers II-VI**). The trueness of the proposed method was judged under the criterion of the significant test score,  $t_{\text{exp}}$ . [95] This parameter is calculated from the reference activity,  $A_{\text{ref}}$ , the measured activity  $A_{\text{mea}}$ , the number of replicates,  $n$ , and the measured standard deviation,  $s_{\text{mea}}$ , as

$$t_{\text{exp}} = \frac{|A_{\text{ref}} - A_{\text{mea}}|}{\sqrt{n} / s_{\text{mea}}}$$

$t_{\text{exp}}$  values were in all instances lower than the  $t_{\text{crit}}$  at the 0.05 significance level, which revealed the inexistence of significant differences between experimental and reference concentrations of plutonium and neptunium for the reference materials regardless the analytical method applied (see Table 7). Moreover, the wide applicability to distinct environmental samples (viz., soil, sediment, plant tissues, seawater, etc...) with satisfactory results demonstrates the flexibility of the SI-based analytical methods proposed in this study.

### 3.4.4 Sample throughput

The proposed SI-based on-column separations in this study take 1.5-3.5 h per sample depending on the chromatographic methods. Thus, >10 samples can be processed in an automated mode within 1.5 day and in parallel with the manual pre-treatment of the next batch of 10 samples in a batch-wise fashion. Compared with the tedious and labor-intensive traditional radionuclide assays, better sample throughput is herein achieved. In addition, the SI-based multi-stage analytical procedure performed stably and robustly within a long-term continuous operation suggesting its actual applicability to the rapid analysis of large number of samples within a short time frame. This meets perfectly the requirement in environmental risk assessment tasks and radiochemical analysis in emergency situations.

Table 7. Analytical results of reference materials using distinct analytical methods developed in this study

Method <sup>†</sup>	Analytical performance	IAEA-375 soil	IAEA-135 sediment	IAEA-385 sediment	Irish sea sediment	NIST-4359 seaweed
AG 1- $\times$ 4-Pu	Chemical yield, %	89.3 $\pm$ 3.5	69.3 $\pm$ 2.5	-	59.2 $\pm$ 5.1	72.5 $\pm$ 3.1
	Measured concentration, <sup>239</sup> Pu	0.12 $\pm$ 0.02 [0.61]	125.9 $\pm$ 8.6 [0.58]	-	228.9 $\pm$ 4.0 [3.51]	0.079 $\pm$ 0.003 [2.89]
	Bq/kg, <sup>240</sup> Pu	0.13 $\pm$ 0.02 [0.52]	95.4 $\pm$ 8.3 [0.33]	-	172.3 $\pm$ 9.0 [1.67]	0.052 $\pm$ 0.005 [1.73]
TEVA-Pu	Chemical yield, %	0.30 $\pm$ 0.04 [0.00]	221.4 $\pm$ 16.9 [0.86]	-	401.7 $\pm$ 12.0 [2.50]	0.131 $\pm$ 0.008 [0.30]
	Measured concentration, <sup>239</sup> Pu	84.4 $\pm$ 10.2	79.7 $\pm$ 7.6	-	85.7 $\pm$ 15.9	82.8 $\pm$ 4.0
	Bq/kg, <sup>240</sup> Pu	0.14 $\pm$ 0.02 [2.34]	126.2 $\pm$ 4.5 [1.23]	-	225.9 $\pm$ 6.2 [3.10]	0.079 $\pm$ 0.001 [1.24]
TEVA-Pu and Np	Chemical yield, %	0.16 $\pm$ 0.02 [3.12]	93.8 $\pm$ 3.6 [0.00]	-	201.3 $\pm$ 54.9 [0.64]	0.052 $\pm$ 0.005 [0.35]
	Measured concentration, <sup>237</sup> Np	0.30 $\pm$ 0.02 [0.00]	220.0 $\pm$ 7.9 [1.53]	-	427.2 $\pm$ 56.6 [0.58]	0.131 $\pm$ 0.005 [0.35]
	Bq/kg, <sup>240</sup> Pu	-	59.7 $\pm$ 6.9	-	64.7 $\pm$ 15.9	56.4 $\pm$ 2.0
AG 1- $\times$ 4-Np	Chemical yield, %	-	0.78 $\pm$ 0.04 [2.86]	-	1.02 $\pm$ 0.04 [1.43]	0.000134 $\pm$ 0.000020 [3.38]
	Measured concentration, <sup>237</sup> Np	-	125.7 $\pm$ 5.4 [0.87]	-	223.7 $\pm$ 7.3 [3.16]	0.079 $\pm$ 0.003 [1.73]
	Bq/kg, <sup>240</sup> Pu	-	93.6 $\pm$ 2.6 [0.13]	-	191.3 $\pm$ 5.9 [3.02]	0.052 $\pm$ 0.005 [1.73]
AG MP-1M-Pu and Np	Chemical yield, %	-	229.3 $\pm$ 8.0 [3.53]	-	415.0 $\pm$ 12.2 [0.57]	0.131 $\pm$ 0.008 [0.30]
	Measured concentration, <sup>237</sup> Np	-	0.93 $\pm$ 0.05 [2.91]	-	0.99 $\pm$ 0.04 [0.13]	-
	Bq/kg, <sup>240</sup> Pu	-	-	-	-	-
Expected concentration*, Bq/kg	Chemical yield, %	-	72.1 $\pm$ 4.2	74.4 $\pm$ 4.2	69.0 $\pm$ 5.1	68.4 $\pm$ 3.3
	Measured concentration, <sup>237</sup> Np	-	0.91 $\pm$ 0.06 [1.85]	0.023 $\pm$ 0.006 [1.27]	0.99 $\pm$ 0.05 [0.10]	0.00020 $\pm$ 0.00006 [0.75]
	Bq/kg, <sup>240</sup> Pu	-	127 $\pm$ 5 [1.39]	1.7 $\pm$ 0.2 [1.91]	230 $\pm$ 7 [1.73]	0.081 $\pm$ 0.002 [2.60]
Expected concentration*, Bq/kg	Chemical yield, %	-	97 $\pm$ 3 [1.85]	1.1 $\pm$ 0.1 [1.39]	183 $\pm$ 2 [1.73]	0.055 $\pm$ 0.006 [0.58]
	Measured concentration, <sup>237</sup> Np	-	224 $\pm$ 7 [2.72]	2.8 $\pm$ 0.2 [1.56]	403 $\pm$ 9 [3.08]	0.136 $\pm$ 0.008 [0.14]
	Bq/kg, <sup>240</sup> Pu	-	0.846 $\pm$ 0.045 <sup>d</sup> (ref 89)	0.0186 $\pm$ 0.0038 <sup>d</sup> (ref 97)	0.987 $\pm$ 0.048 <sup>d</sup> (ref 89)	0.000173 (0.000152-0.000198) <sup>e</sup>
Expected concentration*, Bq/kg	Chemical yield, %	-	123.0 $\pm$ 3.8 <sup>d</sup> (ref 89)	1.92 (1.30-2.07) <sup>e</sup>	237.0 $\pm$ 5.0 <sup>d</sup> (ref 89)	0.0840 $\pm$ 0.0033 <sup>a</sup>
	Measured concentration, <sup>237</sup> Np	-	93.8 $\pm$ 2.3 <sup>d</sup> (ref 89)	1.18 (0.97-1.32) <sup>e</sup>	181.0 $\pm$ 4.9 <sup>d</sup> (ref 89)	0.057 (0.049-0.066) <sup>e</sup>
	Bq/kg, <sup>240</sup> Pu	-	0.124 $\pm$ 0.020 <sup>d</sup> (ref 96)	2.98 (2.81-3.13) <sup>b</sup>	419.0 $\pm$ 10.6 <sup>d</sup> (ref 89)	0.1296 $\pm$ 0.0075 <sup>a</sup>

<sup>†</sup> Values are the average of four replicates ( $\pm$  standard deviation) for AG 1- $\times$ 4-Np and AG MP-1M-Pu and Np methods and the average of three replicates ( $\pm$  standard deviation) for the other methods. <sup>‡</sup> Numbers in brackets are  $1t_{exp}$ -values at the 95% probability level. The critical  $t$ -value ( $t_{crit}$ ) is 3.18 for  $n=4$  and 4.30 for  $n=3$ , respectively. <sup>§</sup> The information value of <sup>237</sup>Np in the certification of NIST-4359 seaweed provided by Risø-DTU, however, the unit for <sup>237</sup>N activity was incorrectly presented in the certification datasheet. The correct value should be 0.17 mBq/kg with a range of 0.152 - 0.198 mBq/kg. <sup>\*</sup> Expected values include <sup>a</sup> certified value, <sup>b</sup> recommended value, <sup>c</sup> information value, <sup>d</sup> literature value, <sup>e</sup> added to the sample



### 3.4.5 Significant characteristics of SI-based protocols

The automated processing of samples in programmable SI-based setups is mechanically simple and effectively expedites the assays of plutonium and neptunium. The employment of precise digital syringe pumps as liquid drivers fosters the implementation of flow programming protocols which enhances method repeatability as a consequence of the precise control of sample and reagent volumes and flow rates within the SI network. The SI system could be reconfigured for different analytical purposes due to the instrumental flexibility, robustness and ease with which hydrodynamic variables can be computer programmed.

For chromatographic separations, samples, washing solutions and eluents can be all nested around a multi-position selection valve in the SI setup, and the execution of most analytical stages is automatically preformed in a closed system with minimum analyst intervention. Consequently, the safety of the analyst, which is one of the major concerns in radio-assays, will be significantly improved. With the merit of using downscaled chromatographic columns for large-sized environmental samples, a low consumption of acidic reagents and reduced generation of radioactive wastes are achieved. These analytical methods thus show green chemical credentials. The reuse of separation columns following appropriate washing sequences also gives rise to cost-effective approaches.

Table 8. Comparison of analytical performance between extraction and anion exchange chromatographic methods developed in this study for determination of plutonium and neptunium in environmental samples

	Extraction chromatography	Anion exchange chromatography
Price of resin	High (e.g. 5600 €/500 g)	Relatively Low (e.g. 330 €/500 g)
Pre-treatment time	16 hr/4-16samples	16 hr/4-16samples
Separation time	1.5 hr/sample	3.5 hr/sample
Measurement time	0.5 hr/sample (including sample preparation)	0.5 hr/sample (including sample preparation)
Chemical yields	80-100% (Pu), 40-80% (Np&Pu)	80-100% (Pu), 70-90% (Np&Pu, AG-MP-1M resin)
Accuracy	High (RSD $\leq$ 5%)	Medium (RSD $\leq$ 10%)
Decontamination	High ( $1-10 \times 10^4$ for $^{238}\text{U}$ )	Medium ( $1-10 \times 10^3$ for $^{238}\text{U}$ )
Consumption of chemicals	Low (e.g. 10 mL of conc. $\text{HNO}_3$ /sample)	High (e.g. 80 mL of conc. $\text{HNO}_3$ /sample)

## 4 Conclusions and perspectives

The developed methods in this study afford reliable and expedite assays, which support the goals of this PhD project. Small-sized chromatographic columns (ca. 2 mL) suffice to provide chemical yields of plutonium > 85% throughout the work regardless the type of sorbent/chromatographic material. In the cases of simultaneous determination of plutonium and neptunium using  $^{242}\text{Pu}$  as a tracer, satisfactory plutonium and neptunium chemical yields and good agreement between chemical yields of  $^{242}\text{Pu}$  and  $^{237}\text{Np}$  are obtained using a macro-porous anion exchanger (AG MP-1M). AG 1-  $\times$  4 anion exchanger shows lower chemical yields for Np, although it is still applicable for determination of neptunium using plutonium as a non-isotopic tracer coupling chemical yields calibration. More than 10 samples can be processed in an automated mode within 1.5 day and in parallel with the manual pre-treatment of the next batch of 10 samples. Compared with the traditional manual methods wherein 2-3 days are normally required for processing similar sample amounts, sample throughput in this study is improved. Therefore, the proposed SI-based analytical methods using a downscaled extraction or anion exchange chromatographic column should be regarded as appealing approaches for rapid determination of plutonium and neptunium at environmentally relevant levels. In addition, the automatization of separation process reduces the man-power, which also makes the chemical separation can be automated operated for overnight, therefore improved the analytical capacity and efficiency.

A brief comparison of the analytical performance between extraction and anion exchange chromatographic methods developed in this study is summarized in Table 8. Generally, the cost of anion exchangers are relatively lower compared with TEVA resins which might make anion exchange methods relatively cost-effective and more suitable for long-term routine analysis. But the higher selectivity of TEVA facilitates quick column separation and, therefore, better sample throughput, lower consumption of chemicals, higher decontamination factors for  $^{238}\text{U}$  and, thus, superior accuracy of the method. Therefore, it may be concluded that selection of an optimum analytical method for plutonium and neptunium determination in a specific situation should be related to the analytical requirements including degree of accuracy, target analytes, number of samples, demanded analytical time-frame as well as sample characteristics. For example, extraction chromatographic methods are more suitable for samples containing higher level of uranium and macro-porous anion exchanger-based method is well suited for simultaneous determination of plutonium and neptunium using plutonium isotope as a tracer.

Automated radiochemical analysis is a field of research which still is rather fresh and thus possesses the attractive power in the future research. As future work, it is worth to devote effort to improve the automation of the analytical procedure from sample pre-treatment to final detection. For example, to automate the essential steps for sample pre-treatment, such as dilution, co-precipitation, filtration and valence adjustment that so far are conducted manually, and to build up an interface for direct and automated detection using in-line inductively coupled plasma mass spectrometry. It is also pivotal to develop multi-nuclides assays and simultaneous processing of samples and broaden the analytical application to various decommissioning wastes, environmental and biological samples.

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## Paper I

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## Review

# Determination of plutonium isotopes in waters and environmental solids: A review

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## ABSTRACT

A number of analytical methods have been developed in the past few years for environmental monitoring of plutonium (Pu) isotopes around nuclear facilities within protocols for emergency preparedness as well as for risk assessment of contaminated areas resulting from nuclear weapon tests, nuclear accidents, and the discharge of nuclear waste. This article summarizes and critically compares recently reported methods for determination of Pu isotopes in waters and environmental solid substrates, in which sample pre-treatment is imperative for separation of the target species from matrix ingredients and/or potentially interfering nuclides prior to detection by radiometric or mass spectrometric techniques. Also discussed, via representative examples, is the automation of the entire analytical protocol by on-line extraction chromatography and ion exchange chromatography using flow injection (FI) or sequential injection (SI) approaches.

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**Abbreviations:** AMS, accelerator mass spectrometry; EC, electron capture; ETV, electrothermal vaporization; FI, flow-injection; HDEHP, 2-ethylhexyl phosphoric acid; HPLC, high performance liquid chromatography; ICP-MS, inductively coupled plasma-mass spectrometry; ICP-QMS, inductively coupled plasma-quadrupole mass spectrometry; ICP-SFMS, inductively coupled plasma sector field mass spectrometry; LSC, liquid scintillation counter; MS, mass spectrometry; REEs, rare earth elements; RIMS, resonance ionization mass spectrometry; SI, sequential injection; TIMS, thermal ionization mass spectrometry; TOA, trioctylamine-xylene; TOPO, tri-*n*-octylphosphine oxide; TTA, thenoyl trifluoroacetone.

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## 1. Introduction

### 1.1. Sources and distribution of Pu in the environment

Pu isotopes are regarded as highly hazardous pollutants in the environment due to their radiological toxicities and very long radioactive half-lives, which lead to long-term persistence in the environment [1,2]. Among the 20 isotopes of Pu with mass numbers ranging from 228 to 247, as presented in Table 1,  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$  and  $^{241}\text{Pu}$  with half-lives of 87.7 year, 24,110 year, 6561 year and 14.35 year, respectively, are the most frequently monitored in environmental studies [3]. Pu isotopes are released into the environment as a result of human nuclear activities including nuclear weapons testing and accidents, satellites and reactors accidents (e.g., Systems for Nuclear Auxiliary Power generator (SNAP) in 1964; Palomares in 1966; Thule in 1968 and Chernobyl in 1986) and discharges from nuclear reprocessing facilities and nuclear power plants as well [4–20]. As shown in Table 2, Pu liberated in nuclear weapons testing, particularly in the late 1950s and early 1960s, is by far the largest source of Pu in the environment, from which the total fallout of 330 TBq of  $^{238}\text{Pu}$ , 7.4 PBq of  $^{239}\text{Pu}$ , 5.2 PBq of  $^{240}\text{Pu}$ , 170 PBq of  $^{241}\text{Pu}$  and 16 TBq of  $^{242}\text{Pu}$  were estimated in 1989 [4]. However, the distribution characteristics of Pu are strongly influenced by the occurrence in different environmental compartments, such as atmosphere, terrestrial environment, aquatic environment, and the concentrations of Pu isotopes might vary with the location of the sites and transportation within and between environmental media. Table 3 summarizes the distribution of  $^{238}\text{Pu}$  and  $^{239+240}\text{Pu}$  in some specific oceans and locations related to nuclear accidents.

### 1.2. Solution chemical behaviour of Pu

Pu ions in solution commonly exist in Pu(III), Pu(IV), Pu(V) and Pu(VI) oxidation states, and each oxidation state can be prepared and stabilized in solution under appropriate conditions [28]. The chemical properties of Pu change to large extent depending on the oxidation state. Pu ions in the lower oxidation states (III and IV) are more stable under acid conditions, yet Pu(VI) is more stable under alkaline media. Pu(IV) is the most stable and studied oxidation state, followed by Pu(III) and Pu(VI). Under non-complexing strongly acidic conditions, such as perchloric or trifluoromethane-

sulfonic acid (triflic acid) solutions, both Pu(III) and Pu(IV) exist as the simple hydrated (or aquo) ions,  $\text{Pu}^{3+}_{(\text{aq})}$  or  $\text{Pu}^{4+}_{(\text{aq})}$ , retaining their overall formal charge. Pu(V) and Pu(VI) cations have such large positive charges that they immediately hydrolyze in aqueous solution to form dioxocations,  $\text{PuO}_2^+$  and  $\text{PuO}_2^{2+}$ , which are commonly referred to as plutonyl ions.

One of the most complex aspects of the aqueous chemistry of Pu is related to the oxidation–reduction relationships of Pu ions. The corresponding electrochemical potentials of the redox couples of Pu are given in Table 4. The redox couples of Pu(V)/Pu(III), Pu(VI)/Pu(III), Pu(V)/Pu(IV), and Pu(VI)/Pu(IV) are quasireversible or irreversible because they involve the breaking or forming of multiple Pu=O bonds. In contrast, the redox couples between species without forming or breaking of Pu=O bonds, such as Pu(IV)/Pu(III), Pu(VI)/Pu(V), and Pu(VII)/Pu(VI), are reversible. Since the redox couples that connect the four oxidation states (III, IV, V, and VI) are relatively similar, the overall oxidation states might coexist under appropriate solution conditions.

A large number of reagents have been used for the oxidation and reduction of Pu, some of them are summarized in Table 5. The reactions involving formation or rupture of a metal–oxygen bond, as in Pu(IV)/Pu(VI) and Pu(IV)/Pu(V) pairs, are inherently slow. In many cases, the reduction of Pu(VI) to Pu(IV) proceeds through the formation of Pu(V), which then disproportionates to produce Pu(IV) and Pu(VI). Nitrite ion plays an important role in Pu aqueous processing. It is capable of oxidizing Pu(III) to Pu(IV) and of reducing Pu(VI) to Pu(IV). Since most aqueous processes, e.g., ion exchange chromatography and extraction chromatography rely on Pu(IV),  $\text{NaNO}_2$  is frequently employed as a valence adjuster to convert Pu to the tetravalent state. Because the Pu(VI) to Pu(IV) reduction by nitrite is slow, often another reducing agent, such as ferrous ion is also added to increase the rate of the reaction. Hydroxylamine and hydrazine are also suitable reducing agents for plutonium in high oxidation states, because they are non-metallic, yield volatile oxidation products, and tend to react rapidly.

The coordination chemistry of Pu ions is distinctive of exceptionally “hard” Lewis acids. Weak Lewis bases, such as hydrogen sulfide, generate weak complexes with Pu and strong Lewis bases, such as carbonate, fluoride and orthophosphate form very stable complexes. Pu ions have relatively large ionic radii and therefore give rise to complexes with high coordination numbers (8–14). For

**Table 1**  
Nuclear properties of Pu isotopes [3].

	Half-life	Specific activity (Bq g <sup>-1</sup> )	Principal decay mode	Decay energy (MeV)	Example of production method
<sup>238</sup> Pu	87.7 year	6.338 × 10 <sup>11</sup>	α	α 5.499 (70.9%) 5.456 (29.0%)	<sup>242</sup> Cm daughter <sup>238</sup> Np daughter
<sup>239</sup> Pu	2.411 × 10 <sup>4</sup> year	2.296 × 10 <sup>9</sup>	α	α 5.157 (70.77%) 5.144 (17.11%) 5.106 (11.94%) γ 0.129	<sup>239</sup> Np daughter
<sup>240</sup> Pu	6.561 × 10 <sup>3</sup> year	8.401 × 10 <sup>9</sup>	α	α 5.168 (72.8%) 5.124 (27.1%)	Multiple n capture
<sup>241</sup> Pu	14.35 year	3.825 × 10 <sup>12</sup>	β <sup>-</sup> > 99.99%	α 4.896 (83.2%) 4.853 (12.2%) β <sup>-</sup> 0.021 γ 0.149	Multiple n capture
<sup>242</sup> Pu	3.75 × 10 <sup>5</sup> year	1.458 × 10 <sup>8</sup>	α	α 4.902 (76.49%) 4.856 (23.48%)	Multiple n capture
<sup>244</sup> Pu	8.08 × 10 <sup>7</sup> year	6.710 × 10 <sup>5</sup>	α 99.88%	α 4.589 (81%) 4.546 (19%)	Multiple n capture

**Table 2**  
Sources of Pu in the environment (Bq).

Radionuclide	<sup>238</sup> Pu	<sup>239</sup> Pu	<sup>240</sup> Pu	<sup>241</sup> Pu	<sup>242</sup> Pu	<sup>239+240</sup> Pu	Total
Nuclear weapons testing [4,21]	3.3 × 10 <sup>14</sup>	6.5 × 10 <sup>15</sup>	4.4 × 10 <sup>15</sup>	1.4 × 10 <sup>17</sup>	1.6 × 10 <sup>13</sup>	12.6 × 10 <sup>15</sup>	1.7 × 10 <sup>17</sup>
Burn up of SNAP-9A satellite [22]	6.3 × 10 <sup>14</sup>	–	–	–	–	–	6.3 × 10 <sup>14</sup>
Aircraft accident in Palomares [5]	–	–	–	–	–	5.5 × 10 <sup>10</sup>	5.5 × 10 <sup>10</sup>
Aircraft accident in Thule, Greenland, 1968 [15,16]	–	–	–	–	–	1 × 10 <sup>13</sup>	1 × 10 <sup>13</sup>
Nuclear power plant accident in Chernobyl, 1986 [23]	3.5 × 10 <sup>13</sup>	3 × 10 <sup>13</sup>	4.2 × 10 <sup>13</sup>	6 × 10 <sup>15</sup>	7.0 × 10 <sup>10</sup>	7.2 × 10 <sup>13</sup>	6 × 10 <sup>15</sup>
Reprocessing plant in Sellafield site [24,25]	1.2 × 10 <sup>14</sup>	–	–	2.2 × 10 <sup>16</sup>	–	6.1 × 10 <sup>14</sup>	2.2 × 10 <sup>16</sup>
Reprocessing plant in La Hague site [26]	2.7 × 10 <sup>12</sup>	–	–	1.2 × 10 <sup>14</sup>	1.7 × 10 <sup>9</sup>	3.4 × 10 <sup>12</sup>	1.4 × 10 <sup>14</sup>
Savannah River Site, 1954–1989 [27]	Release to air	–	–	–	–	–	1.4 × 10 <sup>11</sup>
	Discharge to water	–	–	–	–	–	2.3 × 10 <sup>10</sup>
	Discharge to soil	–	–	–	–	–	2 × 10 <sup>11</sup>

**Table 3**  
<sup>238</sup>Pu and <sup>239+240</sup>Pu concentrations in oceans and given locations after nuclear accidents.

Area		<sup>238</sup> Pu	<sup>239,240</sup> Pu
Surface water of Pacific Ocean [28], Bq L <sup>-1</sup>		–	(0.5–2.8) × 10 <sup>-6</sup>
Surface water of the Sea of Japan [28], Bq L <sup>-1</sup>		–	(5.2 ± 0.9) × 10 <sup>-6</sup>
Surface water of Indian Oceans [28], Bq L <sup>-1</sup>		–	(0.8–2.2) × 10 <sup>-6</sup>
Water in the Baltic Sea [29], Bq L <sup>-1</sup>		–	(0.6–6) × 10 <sup>-6</sup>
Water in the Irish Sea [30], Bq L <sup>-1</sup>		–	(1.0–3.8) × 10 <sup>-3</sup>
Lower Rhone valley (Southern France) [17]	Soil, Bq m <sup>-2</sup>	1.4 ± 0.1	47.0 ± 3.4
	Fruit, Bq kg <sup>-1</sup>	1.5 × 10 <sup>-5</sup>	5 × 10 <sup>-4</sup>
	Leaf vegetables, Bq kg <sup>-1</sup>	7 × 10 <sup>-5</sup>	2.3 × 10 <sup>-3</sup>
	Fruit vegetables, Bq kg <sup>-1</sup>	1.8 × 10 <sup>-5</sup>	6 × 10 <sup>-4</sup>
	Grape (wine), Bq kg <sup>-1</sup>	1.5 × 10 <sup>-5</sup>	5 × 10 <sup>-4</sup>
	Rice, Bq kg <sup>-1</sup>	7 × 10 <sup>-6</sup>	1.7 × 10 <sup>-4</sup>
	Wheat, Bq kg <sup>-1</sup>	4 × 10 <sup>-6</sup>	1.3 × 10 <sup>-4</sup>
	Forages, Bq kg <sup>-1</sup>	3 × 10 <sup>-5</sup>	1.0 × 10 <sup>-3</sup>
Marine environment at Thule, NW-Greenland [19]	Seawater, Bq L <sup>-1</sup>	–	(5–30) × 10 <sup>-6</sup>
	Seaweed, Bq kg <sup>-1</sup>	–	0.15–1.14
	Sediment in surface 0–3 cm layer, Bq kg <sup>-1</sup>	–	0.12
Palomares accident, 1966	Surface soil-1966 [5], Bq m <sup>-2</sup>	–	(1.2–120) × 10 <sup>4</sup>
	Surface soil-2001 [19], Bq m <sup>-2</sup>	–	8–57900
	Air-1966 Mean [5], Bq m <sup>-3</sup>	–	(1.48–4.44) × 10 <sup>-5</sup>
	Air-1967 Mean [5], Bq m <sup>-3</sup>	–	(3.7–444) × 10 <sup>-6</sup>
Chernobyl accident [31], 1986	Air within 30-km zone of the reactor, Bq m <sup>-2</sup>	–	>4000
	Air in Gomel-Mogilev-Bryansk area (200 km north-northeast of the reactor), Bq m <sup>-2</sup>	–	70–700
	Air in Kaluga-Tula-Orel area (500 km northeast of the reactor), Bq m <sup>-2</sup>	–	70–300
	Air in Korosten (115 km southwest of the reactor), Bq m <sup>-2</sup>	–	60

**Table 4**

Electrochemical potentials for redox couples related to plutonium ions in acidic, neutral, and alkaline aqueous solution versus the standard hydrogen electrode [3].

Couple	Acidic	Neutral	Alkaline
Pu(IV)/Pu(III)	+0.982	−0.39	−0.96
Pu(V)/Pu(IV)	+1.170	+0.70	−0.67
Pu(VI)/Pu(V)	+0.913	+0.60	+0.12
Pu(VI)/Pu(IV)	+1.043	+0.65	+0.34
Pu(V)/Pu(III)	–	+1.076	–
Pu(VII)/Pu(VI)	–	–	+0.85

a given ligand the strength of complexes and the liability of ions to hydrolyze decrease following the effective charges:



In many cases, the processing of samples for separation of Pu is carried out in  $\text{HNO}_3$  or  $\text{HCl}$  media. Therefore, the knowledge of complexing behaviour of Pu ions with  $\text{NO}_3^-$  and  $\text{Cl}^-$  is imperative. Table 6 shows the formation of complexes of Pu ions with  $\text{NO}_3^-$  and  $\text{Cl}^-$ . It should be however noticed that the stability constants of  $\text{Pu}^{3+}$  complexes with  $\text{NO}_3^-$  are rather questionable because of Pu(III) ions are most likely oxidated in a  $\text{HNO}_3$  medium.

### 1.3. General analytical procedure for determination of Pu

Because of the potential hazards of Pu isotopes on mankind health, the accurate and reliable determination of these radionuclides in environmental samples is important for (i) environmental risk assessment and monitoring of the environment around nuclear facilities, such as nuclear power plants, nuclear fuel reprocessing plants and nuclear waste storage sites; (ii) emergency preparedness; and (iii) surveillance of contaminated areas from nuclear weapon tests, nuclear accidents, and discharges of nuclear wastes. So far, a large number of analytical methods have been devised and exploited for the determination of Pu in various environmental samples, such as soil, sediment, air-borne particulate matter, seawater, groundwater, surface water and wastewater. In general, the whole procedure, as presented schematically in Fig. 1, can be divided into four steps: initial sample pre-treatment, chemical separation or purification, source preparation, and detection. Different approaches utilized in each step are discussed in the body of the text with relevant examples taken from articles published over the past few years.

Attention is also paid to recent trends in automation of the entire analytical procedure via flow-based approaches. Flow injection (FI) analysis, and related techniques thereof, e.g., sequential injection

(SI) analysis, represent a well documented tool for mechanization of analytical assays, with numerous applications in the biochemical, environmental, clinical, and process analysis fields [33–37]. The inherent features of SI in terms of versatility, self-adaptation, full computer control, minimum consumption of sample and reagents, minute waste generation and instrumental robustness make it very attractive for automation and simplification of various sample processing techniques, including liquid–liquid (micro)extraction and solid-phase extraction (SPE) [38–44]. In fact, a vast number of on-line FI/SI-SPE methods have been recently developed for the analysis of environmental samples contaminated with Pu. Considering the type of SPE columns utilized in the separation procedure, these analytical methods can be sorted into two categories, i.e. FI/SI-based extraction chromatography and FI/SI-based ion-exchange chromatography, which are overviewed in this paper as well.

## 2. Sample pre-treatment

### 2.1. Solid sample

#### 2.1.1. Initial sample processing

At the beginning of the pre-treatment of solid samples (e.g., soil, sediment) large materials with diameters  $>2$  mm (e.g., gravel and plant roots) should be removed by sieving. Solid samples are usually dried at  $60$ – $105^\circ\text{C}$  [45–51] and then ground and further sieved before ensuing treatments. Organic matter in the solid samples can be decomposed by dry ashing in muffle furnaces at  $400$ – $700^\circ\text{C}$  for  $2$ – $24$  h [45,49,52,53]. A tracer should be added to the sample before analysis in order to estimate the chemical yield of Pu isotopes during the analytical procedure. The tracer ideally needs to be preferably measured by the same detection technique as the analyte. In the case of Pu determination,  $^{242}\text{Pu}$  (sometimes  $^{236}\text{Pu}$  or  $^{244}\text{Pu}$ ), an alpha-particle emitter, is often used as the tracer because it is normally not found in significant quantity in environmental samples, and is not a dominant constituent of nuclear fuels or waste waters.

#### 2.1.2. Sample digestion

Before further chemical separation, Pu isotopes should be released from the sample matrix into solution. The ash is frequently decomposed either by acid digestion or alkali fusion. Acid digestion is normally performed in a chemical resistant beaker on a hotplate at atmospheric pressure or in a closed digestion vessel at elevated pressures and temperatures in a microwave oven. Two common methods for releasing of Pu are acid leaching (partial digestion) and total dissolution. In most cases of acid leaching, concentrated

**Table 5**

Reagents for oxidation and reduction of plutonium ions [32].

Reaction	Reagent	Conditions		Rate
		Solution	Temperature	
Pu(III) to Pu(IV)	$\text{HNO}_2$	Moderately concentrated acid	Room temp.	Rapid
	$\text{H}_2\text{O}_2$	Various	Room temp.	Depends on conditions
	$\text{NO}_3^-$	Diluted acid	Room temp.	Extremely slow
	$\text{NaNO}_2$	$0.5 \text{ mol L}^{-1} \text{ HCl}$	$100^\circ\text{C}$	$<1$ min
Pu(IV) to Pu(III)	Hydroquinone	Diluted $\text{HNO}_3$	Room temp.	Rapid
	Ascorbic acid	Moderately concentrated $\text{HNO}_3$ ( $4.75 \text{ mol L}^{-1}$ )	Room temp.	Very rapid if $\text{H}_2\text{SO}_4$ present, otherwise reacts with $\text{HNO}_3$
	$\text{NH}_2\text{OH}$	$0.2 \text{ mol L}^{-1}$ chloride salt	Room temp.	Completed in 5 min
	$\text{N}_2\text{H}_4$	$0.02 \text{ mol L}^{-1}$ sulphate salt	Room temp.	34% completed in 5 min
	$\text{I}^-$	$0.1 \text{ mol L}^{-1} \text{ HI}$ , $0.4 \text{ M HCl}$	Room temp.	Rapid
	$\text{Fe}^{2+}$	Diluted acid	Room temp.	Rapid
	$\text{Ti}^{3+}$	$\text{HCl}$	Room temp.	Rapid
Pu(VI) to Pu(IV)	$\text{Fe}^{2+}$	$\text{HCl}$	Room temp.	Rapid
	$\text{HNO}_2$	$0.5 \text{ mol L}^{-1} \text{ HNO}_3$	Room temp.	Very slow
	$\text{H}_2\text{O}_2$	Various	Room temp.	Depends on conditions
	$\text{Ti}^{3+}$	$\text{HClO}_4$	Room temp.	Rapid

**Table 6**  
Formation of Pu ions complexes with  $\text{NO}_3^-$  and  $\text{Cl}^-$  [32].

Ion	$\text{HNO}_3$	$\text{HCl}$
$\text{Pu}^{3+}$	$\text{Pu}^{3+} + \text{NO}_3^- \leftrightarrow \text{Pu}(\text{NO}_3)^{2+}$ , $K_1 = 5.9 \pm 0.5^a$ $\text{Pu}(\text{NO}_3)^{2+} + \text{NO}_3^- \leftrightarrow \text{Pu}(\text{NO}_3)_2^+$ , $K_2 = 14.3 \pm 0.8^a$ $\text{Pu}(\text{NO}_3)_2^+ + \text{NO}_3^- \leftrightarrow \text{Pu}(\text{NO}_3)_3$ , $K_3 = 14.4 \pm 0.8^a$	$\text{Pu}^{3+} + \text{Cl}^- \leftrightarrow \text{PuCl}^{2+}$ , $K_1 = 4.9 \times 10^{-3}^b$ $\text{PuCl}^{2+} + \text{Cl}^- \leftrightarrow \text{PuCl}_2^+$ , $K_2 = 2.5 \times 10^{-3}^c$
$\text{Pu}^{4+}$	$\text{Pu}^{4+} + \text{NO}_3^- \leftrightarrow \text{Pu}(\text{NO}_3)^{3+}$ , $K_1 = 5.5 \pm 0.2^d$ $\text{Pu}(\text{NO}_3)^{3+} + \text{NO}_3^- \leftrightarrow \text{Pu}(\text{NO}_3)_2^{2+}$ , $K_2 = 23.5 \pm 0.1^d$ $\text{Pu}(\text{NO}_3)_2^{2+} + \text{NO}_3^- \leftrightarrow \text{Pu}(\text{NO}_3)_3^+$ , $K_3 = 15 \pm 10^d$ $\text{Pu}(\text{NO}_3)_3^+ + \text{NO}_3^- \leftrightarrow \text{Pu}(\text{NO}_3)_4$ $\text{Pu}(\text{NO}_3)_4 + \text{NO}_3^- \leftrightarrow \text{Pu}(\text{NO}_3)_5^-$ $\text{Pu}(\text{NO}_3)_5^- + \text{NO}_3^- \leftrightarrow \text{Pu}(\text{NO}_3)_6^{2-}$	$\text{Pu}^{4+} + \text{Cl}^- \leftrightarrow \text{PuCl}^{3+}$ , $K_1 = 1.4 \pm 0.2^d$ $\text{PuCl}^{3+} + \text{Cl}^- \leftrightarrow \text{PuCl}_2^{2+}$ , $K_2 = 1.2 \pm 0.2^d$ $\text{PuCl}_2^{2+} + \text{Cl}^- \leftrightarrow \text{PuCl}_3^+$ , $K_3 = 0.1 \pm 0.1^d$ $\text{PuCl}_3^+ + \text{Cl}^- \leftrightarrow \text{PuCl}_4$ $\text{PuCl}_4 + \text{Cl}^- \leftrightarrow \text{PuCl}_5^-$ $\text{PuCl}_5^- + \text{Cl}^- \leftrightarrow \text{PuCl}_6^{2-}$
$\text{PuO}_2^{2+}$	$\text{PuO}_2^{2+} + \text{NO}_3^- \leftrightarrow \text{PuO}_2(\text{NO}_3)^+$ $\text{PuO}_2(\text{NO}_3)^+ + \text{NO}_3^- \leftrightarrow \text{PuO}_2(\text{NO}_3)_2$ $\text{PuO}_2(\text{NO}_3)_2 + \text{NO}_3^- \leftrightarrow \text{PuO}_2(\text{NO}_3)_3^-$	$\text{PuO}_2^{2+} + \text{Cl}^- \leftrightarrow \text{PuO}_2\text{Cl}^+$ , $K_1 = 1.25^e$ $\text{PuO}_2\text{Cl}^+ + \text{Cl}^- \leftrightarrow \text{PuO}_2\text{Cl}_2$ , $K_2 = 0.35^e$ $\text{PuO}_2\text{Cl}_2 + \text{Cl}^- \leftrightarrow \text{PuO}_2\text{Cl}_3^{-f}$ $\text{PuO}_2\text{Cl}_3^- + \text{Cl}^- \leftrightarrow \text{PuO}_2\text{Cl}_4^{2-f}$

<sup>a</sup> Under the presence of hydrazine, at  $20 \pm 1^\circ\text{C}$ .

<sup>b</sup> Predominate in  $2\text{--}8\text{ mol L}^{-1}$  HCl solution.

<sup>c</sup> Predominate in  $>8\text{ mol L}^{-1}$  HCl solution.

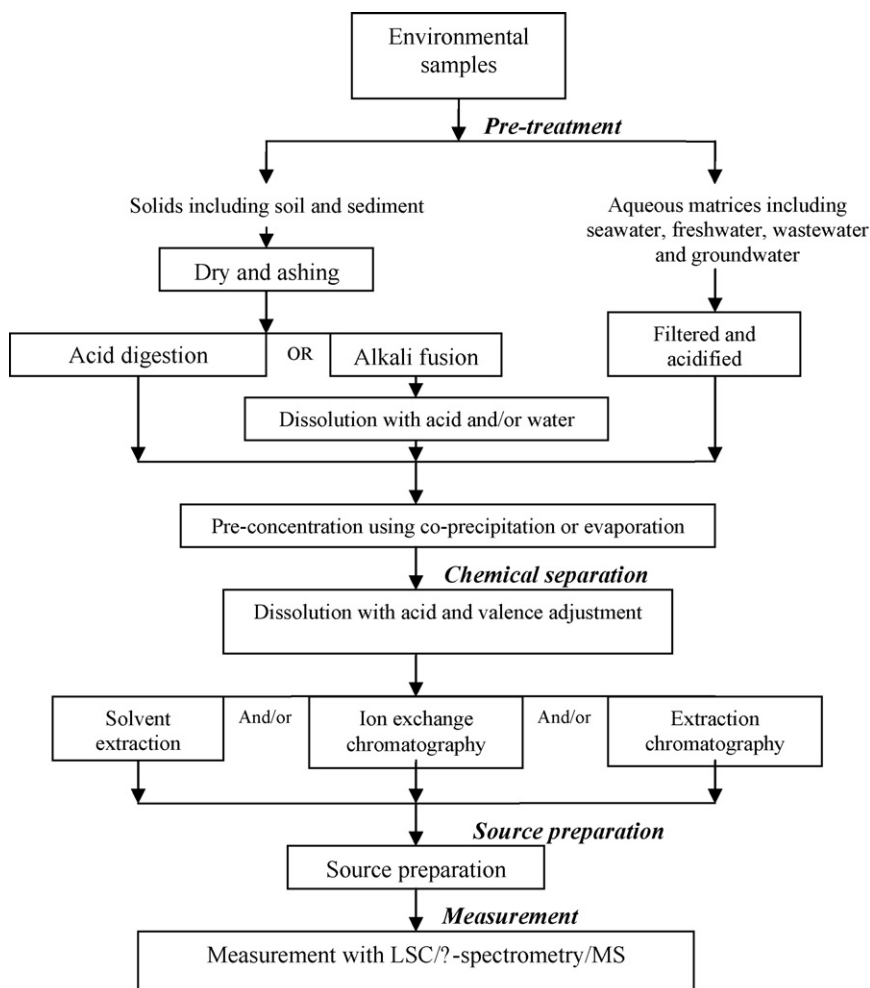
<sup>d</sup> In  $4\text{ mol L}^{-1}$   $\text{HClO}_4$  solution, at  $20^\circ\text{C}$ .

<sup>e</sup> Concentrations of HCl  $< 1\text{ mol L}^{-1}$ .

<sup>f</sup> In  $1\text{ mol L}^{-1}$  HCl solution.

$\text{HNO}_3$  [45,54,55],  $8\text{ mol L}^{-1}$   $\text{HNO}_3$  [56],  $8\text{ mol L}^{-1}$   $\text{HNO}_3\text{--}6\text{ mol L}^{-1}$  HCl [57],  $8\text{ mol L}^{-1}$   $\text{HNO}_3\text{--}6\text{ mol L}^{-1}$   $\text{H}_2\text{O}_2$  [49,58],  $6\text{ mol L}^{-1}$  HCl [47] or aqua regia [59] has been utilized as acid extractants under heat and reflux on a hot plate ( $180\text{--}200^\circ\text{C}$ ) without stirring for 2–6 h. In the case of significant proportions of refractory

Pu oxides (e.g.,  $\text{PuO}_2$ ) in the samples, HF in combination with other acids (e.g.,  $\text{HNO}_3$ , HCl, and  $\text{HClO}_4$ ) can be a choice for total dissolution of the matrix and release of the entire Pu content in the sample [50,60–62]. Aimed at accelerating the digestion speed, improving leaching efficiencies and reducing reagent vol-



**Fig. 1.** Flow chart of the analytical procedure for the determination of Pu in environmental samples.



umes, the application of microwave has attracted the interest of many researchers [49,50,54,58,61,63–65]. Toribio et al. [65], for example, achieved total mineralization of soil and sediment samples in 2.5 h by microwave-assisted dissolution with mixtures of HF–HNO<sub>3</sub> and HF–HClO<sub>4</sub>. However, the experimental results with real samples lead to the conclusion that the implementation of a microwave digestion step prior to chemical separation procedures for Pu caused low recoveries (61 ± 8%). The investigation of potential causes for low Pu recovery demonstrated that the loss of Pu was neither induced by volatilisation whenever HF–HClO<sub>4</sub> mixtures were used, nor related to the presence of fluoride as a potential interference in the digest. Therefore, further studies are needed to focus on the influence of other matrix components on the separation process applied after digestion (see below).

Alkali fusion is an extremely aggressive method performed by heating the sample with a mixture of various fluxes (e.g., hydroxides, peroxides, carbonates, hydrosulfates, pyrosulfates or alkali borates) at atmospheric pressure in a graphite, nickel, zirconium, or platinum crucible [48,66,67]. The mixture is heated to a temperature above the melting point of the flux over a burner or in a muffle furnace until the mixture form a well-mixed molten mass. After cooling, the resulting fusion cake is dissolved with a diluted acid such as HNO<sub>3</sub> or HCl. Croudace et al. [66] described a method in which borate fusion was used for sample pre-treatment. In this method, a eutectic mixture of 80% lithium metaborate and 20% lithium tetraborate was mixed with pre-ignited samples. Fusions were performed in grain-stabilized, Pt–Au (95%/5%) dishes at 1200 °C in a resistance-type furnace. The main safety benefit of the described technique is the limited use of acids and the absence of HF. Warwick et al. [48] applied lithium borate fusion for soil and sediment pre-treatment. The use of this flux permitted the complete dissolution of potentially intractable materials and thus ensured the complete recovery of refractory Pu oxides. They claimed that the lithium borate fusion was preferable to the more conventional HF digestion or fusion with potassium fluoride for safety reasons.

Summing up, acid leaching is not only the simplest method but also suits to the pre-treatment of large sample amounts. However, acid leaching might give rise to poor recoveries for samples containing high proportion of refractory Pu oxides. Although refractory phases hosting Pu are more likely to be extracted by digestion methods using HF, potential dissolution of interfering elements, such as iron, phosphorus, and other rare-earths is also increased. After matrix dissolution HF should be removed either by fuming with HClO<sub>4</sub> or H<sub>2</sub>SO<sub>4</sub> or by complexation with H<sub>3</sub>BO<sub>3</sub> or aluminium in order to facilitate further chemical separations, whereby special extraction facilities for HF vapours and associated safety equipment is needed. Sometimes a combination of the above methods is chosen. A simple way to remove fluoride ions is to dilute the sample and co-precipitate Pu with Fe(OH)<sub>3</sub>, fluoride ions then remain in the aqueous phase. The application of microwave digestion has the advantages of high efficiency, decreased operational time and consumption of reagents, but the sample amount to be digested is limited to a few hundreds of milligrams. In alkali fusion, however, samples are completely decomposed and Pu losses in the residue are kept to minimum. It is therefore one of the most effective methods for digestion of solid sample containing silicates and refractory Pu. Fusion is normally applicable to large sample amounts (several grams) but becomes unreliable when exceeding 5 g, which however in many instances are needed [66,68]. A drawback of the alkaline fusion is the aggressiveness of the reaction that might lead to the addition of crucible components to the sample matrix.

### 2.1.3. Pre-concentration using co-precipitation

Co-precipitation is a traditional method for the pre-concentration and removal of matrix components in sample

extracts or digests following acid leaching/digestion or alkali fusion. The most frequently used reagents for Pu co-precipitation are fluorides (e.g., NdF<sub>3</sub>, LaF<sub>3</sub>, and CeF<sub>3</sub>) [46,61,69], Fe(OH)<sub>2</sub> or Fe(OH)<sub>3</sub> [49,57,67], phosphates (CaHPO<sub>4</sub>, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>) [70], calcium oxalate (CaC<sub>2</sub>O<sub>4</sub>) [45]. Co-precipitation of Pu(IV) with rare earth fluorides (e.g., NdF<sub>3</sub>) is a common method for preliminary separation of Pu [64,66] because co-precipitation of U(VI) is not favoured, and hereby the interfering effects of uranium are lessened. Co-precipitation with Fe(OH)<sub>3</sub> or Fe(OH)<sub>2</sub> [53,63] is the method of choice for isolation of Pu from large volumes of carbonate-free water samples (100–500 L). On the other hand, co-precipitation of Pu(III) and Pu(IV) with CaC<sub>2</sub>O<sub>4</sub> is preferred for those samples containing high concentrations of iron, because iron reacts with oxalic acid within the pH range of 5.5–6.0 to form a soluble chelate. CaF<sub>2</sub>-based co-precipitation [54,71] has been proven effective for isolation of Pu from soils and sediments. In this method, co-precipitation is performed with the addition of Ca(NO<sub>3</sub>)<sub>2</sub> to the acidic extract/digest followed by a reducing agent (NH<sub>2</sub>OH·HCl) and concentrated HF.

Notwithstanding the fact that Fe(OH)<sub>2</sub> or Fe(OH)<sub>3</sub> are the most commonly used co-precipitation reagents for uptake of Pu, CaF<sub>2</sub> and rare earth-fluoride co-precipitations have the advantageous features of being carried out in strong acidic media. Thus, there is no risk of precipitation of the main matrix components (e.g., alkali metals and most transition metals) and possible interfering compounds for chemical separation (e.g., phosphate, sulphate) or detection (e.g., U).

## 2.2. Aqueous samples

### 2.2.1. Filtration and acidification

In order to fractionate Pu between dissolved species and those associated to suspended particulate matter, water samples (e.g., seawater, freshwater, and groundwater) should be filtered through appropriate filters before acidification to pH 1–2. Acidification should be performed immediately after sample collection as hydrolyzed Pu species have great affinity towards exposed surfaces, including the walls of the container. The tracer should be added after acidification as hydrolysis of the tracer can lead to an uneven distribution within the sample.

### 2.2.2. Pre-concentration (evaporation and co-precipitation)

Plutonium is found in environmental waters, e.g., seawater, at much lower concentration levels (typically within the femtograms per litre range) than in other types of environmental samples. Accordingly, large volume sampling and labour-intensive sample pre-treatments are essential for accurate determination of Pu in water. For instance, appropriate method sensitivity is merely achieved whenever sample volumes of 100–200 L water are processed. The analyte should therefore be concentrated to a smaller volume before further chemical separations take place. Evaporation is sometimes used for pre-concentration purposes for samples with low salt content, but it is inadequate for neither processing large sample volumes (>5–10 L) nor samples containing high levels of total dissolved solids, such as seawater. In these circumstances, co-precipitation can be the method of choice for trace level determinations of Pu. Schamloff et al. [72] applied co-precipitation with MnO<sub>2</sub> and Fe(OH)<sub>3</sub> in different steps to pre-concentrate Pu from 10 L tap water down to 125 µL. Fe(OH)<sub>2</sub>, Fe(OH)<sub>3</sub> and MnO<sub>2</sub> have also been extensively used for pre-concentration of Pu from large volumes of freshwater and seawater [62,73]. Chen et al. [73], for example, pre-concentrated Pu in 200 L of seawater by co-precipitation with Fe(OH)<sub>2</sub>. The pH was controlled to 8.5–9.0 during the co-precipitation procedure to minimize the formation of Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> side products. During field-based sampling it might however be advantageous to exploit a large Ca + Mg + Fe

hydroxide precipitate for ease of handling and minimisation of redistribution of precipitate by wind and wave action. In the laboratory the bulky precipitate may be dissolved and again precipitated using ammonium/ammonia buffer up to about pH 8–9 which then causes only  $\text{Fe}(\text{OH})_3$  to precipitate. Norisuye et al. [74] developed a method to pre-concentrate Pu from several thousand litres of seawater using  $\text{MnO}_2$ -impregnated fibers. By this means Pu can be on-board extracted, making the transportation of large volume of seawater unnecessary. The recoveries of  $^{239+240}\text{Pu}$  using  $\text{MnO}_2$ -impregnated fibers (>95%) were higher than those obtained by previous techniques [69]. However, compared to the precipitation with  $\text{Fe}(\text{OH})_2$  and/or  $\text{Fe}(\text{OH})_3$ , the removal of Mn from the final precipitate is frequently somewhat more troublesome.

For both solid and liquid environmental samples, the precipitate containing Pu should be separated by filtration or centrifugation, washed, and dissolved with  $\text{HNO}_3$  or HCl afterwards.

### 2.3. Valence adjustment

In the environment, Pu can coexist in several oxidation states with different chemical behaviours. It is therefore imperative to ensure that the chemical procedure employed does not discriminate between Pu isotopes in the sample and the added tracer as well. To the end, the conversion of the overall Pu to a single oxidation state is usually performed by an unequivocal redox cycle before further chemical separation. Under most conditions, Pu is converted to Pu(IV) and, in some cases, to Pu(III). To this point, a variety of redox reagents have been used, namely,  $\text{NaNO}_2$  [45],  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{NaNO}_2(\text{s})\text{--HNO}_3$  [56],  $\text{H}_2\text{O}_2\text{--Na}_2\text{S}_2\text{O}_3\text{--NaNO}_2$  [73],  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}\text{--NaNO}_2(\text{s})$  [50],  $\text{NH}_2\text{OH} \cdot \text{HCl}\text{--NaNO}_2(\text{s})$  [49], and  $\text{Fe}(\text{NH}_2\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}\text{--ascorbic acid}$  [65] (see Table 5 for further information).

## 3. Chemical separation and purification

The accuracy and precision of most analytical methods for Pu determination are often deteriorated because of non-specific interferences occasioned by more abundant sample matrix species and specific or isobaric interferences from other nuclides. For example,  $^{241}\text{Am}$ , as an alpha emitter with decay energy of 5.443 MeV (13%) and 5.486 MeV (86%), interferes the measurement of  $^{238}\text{Pu}$  (decay energy 5.456 MeV (72%)) by  $\alpha$ -spectrometry, while  $^{238}\text{U}$  often gives rise to tailing and isobaric effects by the formation of polyatomic ions  $^{238}\text{U}^1\text{H}$  and  $^{238}\text{U}^2\text{H}$  during the detection of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ , respectively, using inductively coupled plasma-mass spectrometry (ICP-MS). More details of interferences in the determination of Pu isotopes are given in Table 7. These interferences often necessitate chemical separation of Pu from the interfering species before detection. Additionally, chemical separations are usually designed to concentrate Pu, which is needed in environmental assays because of the low level concentrations of the target radionuclide as commented above. For separation and purification of Pu, a variety of techniques have been used, yet the most common are solvent extraction, ion exchange chromatography, extraction chromatography, high performance liquid chromatography or a combination of two or more methods [3,60]. Table 8

compiles the analytical performance of reported procedures using different separation methods for determination of Pu in waters and environmental solids.

### 3.1. Solvent extraction

Solvent extraction is frequently exploited in the reprocessing of spent fuel and treatment of radioactive waste. Several extraction reagents have been reported for the separation

and pre-concentration of Pu including TOA (trioctylamine)-xylene [51,75], TTA (thenoyltrifluoroacetone)-benzene [74], HDEHP(di-2(ethylhexyl)-phosphoric acid) [76,77] and TOPO (tri-*n*-octylphosphine oxide) [78]. For instance, Norisuye et al. [74] purified Pu from a large volume of seawater by solvent extraction using TTA-benzene. The recoveries of Pu within the solvent extraction stage amounted to  $96 \pm 2\%$ . Momoshima et al. [51] carried out the separation of Pu from pine needle, litter and sediment samples using 10% (w/v) TOA-xylene. Pu in an  $8 \text{ mol L}^{-1} \text{HNO}_3$  medium was extracted with TOA-xylene twice, followed by back-extraction with a  $0.1 \text{ mol L}^{-1} \text{NH}_4\text{I}\text{--}8.5 \text{ mol L}^{-1} \text{HCl}$  solution. In the early days, solvent extraction played an important role for the separation of Pu in environmental samples. Solvent extraction offers the great advantage of selection between numerous extractants whereby the selectivity can be readily modulated, however, it is deemed too labour-consuming for routine analysis because several extractions should be consecutively performed to completely separate the analyte from the bulk solution. Difficulties in phase separation and the mutual solubility of the two phases might result in a significant loss of the analyte. Furthermore, a large volume of residual hazardous organic solvents is obtained. Nowadays, as the rapid development of extraction chromatography and ion exchange chromatography techniques, solvent extraction is not often used as a routine method for chemical separation of Pu in environmental samples. However, it is flexible, and still offers some very attractive features when single samples are analysed. For example, the separation of Pu using solvent extraction with the combination of TBP and TTA, requires less than 1 h for complete separation and making the eluate ready for injection to ICP-MS or  $\alpha$ -spectrometry.

### 3.2. Ion exchange chromatography

Because of the high ionic potential as well as its proclivity to form anionic complexes Pu might be eventually sorbed onto either cation exchangers or anion exchangers. In the presence of ion exchange resins, Pu complexes will exchange with ions of the same charge on the resin if the overall free energy lowered after the exchange. Ion exchange separation using large-size columns is therefore a common technique for isolation of Pu in complex matrices. Due to the pronounced ability of actinides in the higher oxidation states to form anionic complexes, anion exchange chromatography using Dowex 1(or AG 1 or AG MP-1) resins [49,50,56,59,62,73,79], is the most widely accepted method, whereas the cation exchange process is seldom employed [80].

The basis for separation of Pu on an anion-exchanger relies upon the strong sorption of anion complexes of Pu(IV) with  $\text{NO}_3^-$  forming in  $\text{HNO}_3$  medium. Most of the matrix elements cannot form anion complexes under these conditions, and therefore cannot be sorbed on the column. In addition, the III, V and VI oxidation states of Pu and transuranium elements, such as Am, cannot form anionic complexes either. Thorium, like Pu(IV) forms a strong nitrate complex while uranium only forms a weak complex and therefore might be readily separated from Pu by anion-exchange in nitric acid media. A general flow sheet for the chemical separation of Pu via anion-exchange is illustrated in Fig. 2 The separation of Pu from matrix ingredients including radionuclides is generally accomplished by valence adjustment of the target analyte, sample loading onto anion-exchange column in  $7\text{--}8 \text{ mol L}^{-1} \text{HNO}_3$ , washing with  $7\text{--}8 \text{ mol L}^{-1} \text{HNO}_3$  to remove most of the inert matrix species as well as Am and U, washing with  $9\text{--}12 \text{ mol L}^{-1} \text{HCl}$  to remove Th, and finally elution of Pu using reductant-containing diluted  $\text{HNO}_3$  or HCl solution. The latter is preferred since both traces of remaining uranium and Po retain on the resin. In case of solutions containing fluoride, aluminium should

**Table 7**

Comparison of different techniques for detection of Pu isotopes.

Method	Measurable isotope	Interfering species	Detection limit, mBq	Detection time	Accessibility	Cost	Ref.
$\alpha$ -spectrometry	$^{238}\text{Pu}$	$^{241}\text{Am}$ , $^{210}\text{Po}$ , $^{228}\text{Th}$	0.01–0.1	Day-weeks	Good	Fair/high	[26,71,73,123]
	$^{239+240}\text{Pu}$	$^{229}\text{Th}$ , $^{231}\text{Pa}$ , $^{232}\text{U}$ , $^{243}\text{Am}$	0.01–0.1				
	$^{241}\text{Pu}$ ( $^{241}\text{Am}$ )	$^{210}\text{Po}$ , $^{228}\text{Th}$	0.1–1.0				
LSC	$^{241}\text{Pu}$ , $^{238}\text{Pu}$ , $^{239+240}\text{Pu}$	All beta emitters	5–50	Hours	Good	Fair/high	[26,69]
ICP-MS	$^{239}\text{Pu}$	$^{238}\text{U}^{1}\text{H}$ , $^{208}\text{Pb}^{31}\text{P}$ , $^{206}\text{Pb}^{33}\text{S}$ , $^{204}\text{Hg}^{35}\text{Cl}$ , $^{205}\text{Tl}^{34}\text{S}$ , $^{203}\text{Tl}^{36}\text{Ar}$ , $^{202}\text{Hg}^{37}\text{Cl}$ , $^{199}\text{Hg}^{40}\text{Ar}$	0.01–0.1	Hour/min.	Good	Fair/low	[98,124]
	$^{240}\text{Pu}$	$^{238}\text{U}^{2}\text{H}$ , $^{209}\text{Bi}^{31}\text{P}$ , $^{208}\text{Pb}^{32}\text{S}$ , $^{207}\text{Pb}^{33}\text{S}$ , $^{206}\text{Pb}^{34}\text{S}$ , $^{205}\text{Tl}^{35}\text{Cl}$ , $^{204}\text{Pb}^{36}\text{Ar}$ , $^{204}\text{Hg}^{36}\text{Ar}$ , $^{203}\text{Tl}^{37}\text{Cl}$ , $^{200}\text{Hg}^{40}\text{Ar}$	0.01–0.1				
	$^{241}\text{Pu}$	$^{241}\text{Am}$ and any other molecule with identical or similar m/z as $^{241}\text{Pu}$	5–50				
AMS	$^{239}\text{Pu}$	$^{238}\text{U}$ and any other molecule with identical or similar m/z as $^{239}\text{Pu}$	$10^{-4}$ – $10^{-3}$	Hour/min.	Difficult	High	[96,120]
	$^{240}\text{Pu}$	Any other molecule with identical or similar m/z as $^{240}\text{Pu}$	$10^{-4}$ – $10^{-3}$				
	$^{241}\text{Pu}$	$^{241}\text{Am}$ and any other molecule with identical or similar m/z as $^{241}\text{Pu}$	–				
RIMS	$^{239}\text{Pu}$	Matrix elements	0.01–0.1	Hour/min.	Difficult	High	[67,122]
	$^{240}\text{Pu}$		0.01–0.1				
	$^{241}\text{Pu}$		5–50				
TIMS	$^{239}\text{Pu}$	Matrix elements	$10^{-4}$ – $10^{-3}$	Hour/min.	Difficult	High	[121]
	$^{240}\text{Pu}$		$10^{-4}$ – $10^{-3}$				
	$^{241}\text{Pu}$		–				

be added to preferentially complex the fluoride and improve Pu recovery.

Taking into account the different valence states of Pu in environmental samples, a two-step redox procedure is usually needed for selective conversion of the overall Pu into Pu(IV). Chen et al. [73], for example, used  $\text{Na}_2\text{SO}_3$  for initial reduction of Pu to Pu(III), followed by addition of  $\text{NaNO}_2(\text{s})$  or concentrated  $\text{HNO}_3$  to oxidize Pu(III) to Pu(IV). Moreno et al. [50] applied Bio-Rad AG 1  $\times$  8 resin to separate Pu from soil extracts and utilized  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  and  $\text{NaNO}_2(\text{s})$  to convert Pu into Pu(IV).

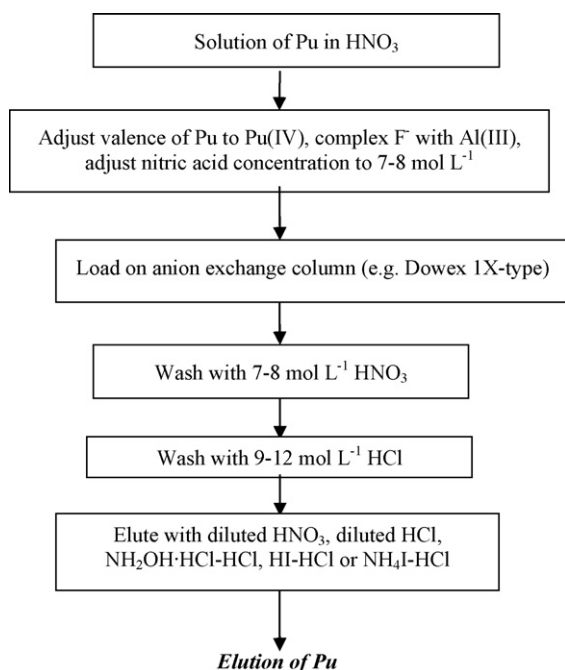
For elution of Pu sorbed onto anion exchangers different kinds of reagents have been exploited. For instance, Sturup et al. [59] used Dowex 1  $\times$  4 resin and elution with  $1.2\text{ mol L}^{-1}$   $\text{HCl}$ –0.6%

$\text{H}_2\text{O}_2$  for separation of Pu in sediments. Diluted iodide (e.g.,  $\text{NH}_4\text{I}$ ,  $\text{HI}$ )– $9\text{ mol L}^{-1}$   $\text{HCl}$  [52,53,56] as well as  $\text{NH}_2\text{OH}\cdot\text{HCl}$  [58,81] have been also employed by several researchers as the eluent of Pu.

Montero et al. [49] compared two separation procedures using Dowex 1  $\times$  8 resin for the determination of Pu in soil samples. In the first procedure, Pu(IV) was stabilized by the addition of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  and  $\text{NaNO}_2(\text{s})$ , and loaded onto the column in  $8\text{ mol L}^{-1}$   $\text{HNO}_3$ . After washing with  $8\text{ mol L}^{-1}$   $\text{HNO}_3$  and  $10\text{ mol L}^{-1}$   $\text{HCl}$ , Pu was eluted with  $0.1\text{ mol L}^{-1}$   $\text{HI}$ – $9\text{ mol L}^{-1}$   $\text{HCl}$ . In the second procedure, Pu was directly converted to Pu(IV) by  $\text{NaNO}_2(\text{s})$  and loaded in  $9\text{ mol L}^{-1}$   $\text{HCl}$ . The column was washed consecutively with  $10\text{ mol L}^{-1}$   $\text{HCl}$  and  $8\text{ mol L}^{-1}$   $\text{HNO}_3$ . Finally, Pu was eluted with  $9\text{ mol L}^{-1}$   $\text{HCl}$ – $\text{H}_2\text{O}_2$ . The first procedure was found to yield higher recoveries than the second one (60% vs. 40%). Besides, a high percentage of Pu appeared in the U and Th fractions in the second procedure, indicating a premature elution of targeted species. The low recovery of the second method might be attributed to the method selected for valence adjustment. In principle,  $\text{NaNO}_2$  can reduce Pu(VI) to Pu(IV) and oxidize Pu(III) to Pu(IV), so can virtually adjust Pu to Pu(IV). Yet, the reduction of Pu(VI) to Pu(IV) needs actually several hours under room temperature for completion if no catalyst is added [82]. With the addition of Fe(II), the reduction of Pu(VI) to Pu(IV) can be promoted [82]. However, because the concentration of Pu in the environmental samples is very low, the reduction of Pu(VI) to Pu(IV) might be still not fast enough to be completed within a few minutes. In this case, the Pu(VI) fraction which is not converted to Pu(IV) is to be lost during the separation. The most suitable procedure for quantitative valence adjustment is the reduction of Pu to Pu(III) with a strong reductant followed by oxidation of the resulting Pu(III) to Pu(IV) by nitrite. This procedure is generally fast enough to convert the overall Pu into Pu(IV) in a few minutes [82].

### 3.3. Extraction chromatography

Extraction chromatography is an extraction and sample clean-up process performed in a continuous and multi-stage manner on a packed column. In this technique the stationary phase consists of one or more ionophores dissolved in an organic solvent which is immobilized on a porous support material. The inert support is normally composed of porous silica or organic polymers with



**Fig. 2.** General flow sheet for separation of Pu using anion exchange chromatography.



**Table 8**  
Comparison of analytical procedures using different separation methods for determination of Pu in environmental samples.

Sample	Separation method	Valence adjustment	Back extraction/eluent	Chemical yield	Detection method	Nuclide	Detection limit	Ref.
Seawater	Solvent extraction using TTA-benzene	6 mol L <sup>-1</sup> NaNO <sub>2</sub>	10 mol L <sup>-1</sup> HNO <sub>3</sub>	96 ± 2%	α-Spectrometry ICP-MS	<sup>239</sup> Pu, <sup>240</sup> Pu, <sup>238</sup> Pu	–	[74]
Plant and sediment	Solvent extraction using TOA-xylene	–	0.1 mol L <sup>-1</sup> NH <sub>4</sub> I–8.5 mol L <sup>-1</sup> HCl HNO <sub>3</sub> , NaNO <sub>3</sub> –HNO <sub>3</sub>	56–73%	α-Spectrometry ICP-MS	<sup>239</sup> Pu, <sup>240</sup> Pu, <sup>238</sup> Pu	–	[51]
Seawater	AG 1 × 4	Na <sub>2</sub> SO <sub>3</sub> –NaNO <sub>2</sub> (s)	–	60–80%	α-Spectrometry	<sup>238</sup> Pu <sup>239</sup> + <sup>240</sup> Pu	–	[73]
Sediment	Dowex 1 × 4	–	1.2 mol L <sup>-1</sup> HCl–0.6% H <sub>2</sub> O <sub>2</sub>	–	SF-ICP-MS	<sup>239</sup> Pu	0.1 mBq	[59]
Soil	AG 1 × 8	(NH <sub>4</sub> ) <sub>2</sub> Fe(SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O–NaNO <sub>2</sub> (s)–HNO <sub>3</sub>	0.1 mol L <sup>-1</sup> NH <sub>4</sub> I–9 mol L <sup>-1</sup> HCl	–	α-Spectrometry AMS	<sup>240</sup> Pu <sup>242</sup> Pu <sup>238</sup> Pu	0.08 mBq 2 μBq –	[56]
Soil	Bio Rad AG 1 × 8	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O–NaNO <sub>2</sub> (s)	0.1 mol L <sup>-1</sup> NH <sub>4</sub> I–9 mol L <sup>-1</sup> HCl	>80%	α-Spectrometry	<sup>239</sup> Pu <sup>240</sup> Pu <sup>238</sup> Pu	–	[50]
Soil	Dowex 1 × 8	NH <sub>2</sub> OH·HCl–1 mol L <sup>-1</sup> HCl–NaNO <sub>2</sub> (s)–8 mol L <sup>-1</sup> HNO <sub>3</sub>	0.1 mol L <sup>-1</sup> HI–9 mol L <sup>-1</sup> HCl	~60%	α-Spectrometry	<sup>239</sup> + <sup>240</sup> Pu <sup>238</sup> Pu	–	[49]
Soil	Dowex 1 × 8	NaNO <sub>2</sub> (s)–1 mol L <sup>-1</sup> HNO <sub>3</sub>	9 mol L <sup>-1</sup> HCl–H <sub>2</sub> O <sub>2</sub>	~40%	α-Spectrometry	<sup>239</sup> + <sup>240</sup> Pu <sup>238</sup> Pu <sup>239</sup> + <sup>240</sup> Pu	–	[49]
Seaweed and sediment	TEVA	25% (w/w) NaNO <sub>2</sub>	0.1 mol L <sup>-1</sup> HNO <sub>3</sub> –0.1 mol L <sup>-1</sup> HF	72–92%	α-Spectrometry SF-ICP-MS SF-ICP-MS SF-ICP-MS	<sup>239</sup> Pu <sup>240</sup> Pu <sup>241</sup> Pu <sup>238</sup> Pu	0.021 mBq 0.014 mBq 11.9 mBq –	[71]
Soil and sediment	TEVA	–	0.5 mol L <sup>-1</sup> HCl	56–73%	α-Spectrometry ICP-MS	<sup>239</sup> + <sup>240</sup> Pu <sup>238</sup> Pu	–	[51]
soil, tank sludge and waste	TRU	NaNO <sub>2</sub> (s)–2 mol L <sup>-1</sup> HNO <sub>3</sub>	0.1 M hydroquinone–4 mol L <sup>-1</sup> HCl	–	α-Spectrometry	<sup>239</sup> + <sup>240</sup> Pu <sup>238</sup> Pu	–	[25]
soil and sediment	UTEVA + TRU	UTEVA: Fe(NH <sub>2</sub> SO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O–ascorbic acid TRU: 0.1 mol L <sup>-1</sup> NaNO <sub>2</sub> –2 mol L <sup>-1</sup> HNO <sub>3</sub>	0.1 mol L <sup>-1</sup> (HN <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	~80%	α-Spectrometry	<sup>239</sup> + <sup>240</sup> Pu <sup>238</sup> Pu <sup>239</sup> + <sup>240</sup> Pu	0.22–1.75 mBq	[65]
Soil and sediment	UTEVA + TRU	UTEVA: Fe(NH <sub>2</sub> SO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O–ascorbic acid TRU: 0.1 mol L <sup>-1</sup> NaNO <sub>2</sub> –4 mol L <sup>-1</sup> HNO <sub>3</sub>	0.1 mol L <sup>-1</sup> (HN <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	~80%	α-Spectrometry SF-ICP-MS	<sup>238</sup> Pu <sup>239</sup> Pu	– 23–58 μBq	[54]
Sediment	TRU + UTEVA + TRU + Sr	1st TRU: NaNO <sub>2</sub> (s)–ascorbic acid UTEVA: Fe(NH <sub>2</sub> SO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O–ascorbic acid 2nd TRU: 0.1 mol L <sup>-1</sup> NaNO <sub>2</sub> –2 mol L <sup>-1</sup> HNO <sub>3</sub>	0.1 mol L <sup>-1</sup> (HN <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	84 ± 6%	SF-ICP-MS SF-ICP-MS α-Spectrometry	<sup>240</sup> Pu <sup>241</sup> Pu <sup>238</sup> Pu <sup>239</sup> + <sup>240</sup> Pu	84–210 μBq 38–36 mBq –	[61]

spent nuclear fuel samples and sediment	CS5A	0.2 mol L <sup>-1</sup> NaNO <sub>2</sub>	2 mol L <sup>-1</sup> HCl	-	ICP-MS	<sup>242</sup> Pu	0.07 Bq mL <sup>-1</sup>	[63]
Soil	PD-DVB	-	0.1 mmol L <sup>-1</sup> dipicolinic acid–1.75 mol L <sup>-1</sup> HNO <sub>3</sub>	-	SF-ICP-MS	<sup>244</sup> Pu <sup>239</sup> Pu	0.3 mBq mL <sup>-1</sup> 18.4 μBq	[49]
Sediment	Bio Rad AG 1 × 8 + solvent extraction using HTTA–xylene + Dowex 1 × 8	BioAG 1 × 8; NaNO <sub>2</sub> –8 mol L <sup>-1</sup> HNO <sub>3</sub>	Bio AG 1 × 8; Na <sub>2</sub> SO <sub>3</sub> –0.8 mol L <sup>-1</sup> HNO <sub>3</sub>	42%	SF-ICP-MS	<sup>239</sup> Pu	460–518 μBq	[58]
		Solvent extraction: Na <sub>2</sub> SO <sub>3</sub>	Solvent extraction: 8 mol L <sup>-1</sup> HNO <sub>3</sub> Dowex 1 × 8; NH <sub>2</sub> OH·HCl–1 mol L <sup>-1</sup> HCl			<sup>240</sup> Pu <sup>241</sup> Pu	630–840 μBq 287–382 mBq	
Soil and sediment	TRU+ anion exchange	-	TRU: 1 mol L <sup>-1</sup> HCl–0.02 mol L <sup>-1</sup> HF Anion exchange: NH <sub>4</sub> I–9 mol L <sup>-1</sup> HCl Chelating resin: 0.1 mol L <sup>-1</sup> HDEHP	40–60%	α-Spectrometry	<sup>242</sup> Pu <sup>244</sup> Pu <sup>238</sup> Pu <sup>239+240</sup> Pu	11–15 μBq 0.13–0.15 μBq –	[48]
Soil	Chelating resin + TRU	TRU: 35% Fe(NH <sub>2</sub> SO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O–0.1 mol L <sup>-1</sup> NaNO <sub>2</sub> (s)–2.5 mol L <sup>-1</sup> HNO <sub>3</sub>		85 ± 5%	α-Spectrometry	<sup>238</sup> Pu	–	[57]
Soil and sediment	Dowex 1 × 8 + TRU + Sr-Spec	Dowex 1 × 8; NH <sub>2</sub> OH·HCl–NaNO <sub>2</sub>	TRU: 0.05 mol L <sup>-1</sup> TiCl <sub>3</sub> –4 mol L <sup>-1</sup> HCl Dowex 1 × 8:	61%	α-Spectrometry	<sup>239+240</sup> Pu <sup>238</sup> Pu <sup>239+240</sup> Pu	–	[55]
Artificial solution	TEVA+ TCC-II + CS5A	TEVA: ascorbic acid–NH <sub>2</sub> OH·HCl	0.1 mol L <sup>-1</sup> I <sup>-</sup> –9 mol L <sup>-1</sup> HCl TEVA: 0.5 mol L <sup>-1</sup> HCl TCC-II: 0.05 mol L <sup>-1</sup> HCl CS5A: 0.018 mol L <sup>-1</sup> dipicolinic acid–0.12 mol L <sup>-1</sup> NaOH–0.27 mol L <sup>-1</sup> CH <sub>3</sub> COOH	–	α-Spectrometry	<sup>239</sup> Pu	–	[87]

particle sizes typically ranging between 50 and 150  $\mu\text{m}$ . Extraction chromatography combines the diversity and selectivity of solvent extraction with the high extraction efficiencies of Column separation.

Over the past few years, extraction chromatography has become a very attractive method for Pu separation in environmental samples [46,51,65,67,70–72] because of short sample processing times, easy operational procedures and the availability of commercial actinides-specific extraction resins, such as TEVA, TRU and UTEVA from Eichrom Technologies in US or Triskem International in Europe. Similar to the ordinary ion exchange resins, a pre-separation protocol might be needed to remove dissolved salts in large sample volumes to maintain the selectivity and capacity of the resin. Yet, the most severe shortcoming is the lack of a Pu-specific sorbent material, whereby the interference of concomitant U, which is frequently found at much higher concentration levels than Pu, cannot be completely overcome merely by exploiting a single extraction column separation. Therefore, the combination of two or more sorbent materials is applied in the case of samples containing high levels of uranium.

### 3.3.1. Single column

TEVA, an extraction chromatographic resin developed by Horwitz et al. [83] and composed of a quaternary amine-based anion exchanger sorbed onto an inert support, has been widely used for uptake of actinides in 2–4  $\text{mol L}^{-1}$   $\text{HNO}_3$  or HCl media. For example, Varga et al. [71] utilized TEVA-based extraction chromatography for the separation of Pu in seaweed and sediments following stabilization of the target species in the tetravalent state. Extracts in 3  $\text{mol L}^{-1}$   $\text{HNO}_3$  were loaded on the resin, followed by consecutive rinsing with 3  $\text{mol L}^{-1}$   $\text{HNO}_3$  and 6  $\text{mol L}^{-1}$  HCl. Pu was eluted by 0.1  $\text{mol L}^{-1}$   $\text{HNO}_3$ –0.1  $\text{mol L}^{-1}$  HF. The proposed method eliminated the eventual interferences of Th, Am, U, Pb and Bi in the final detection step. The decontamination factors (the ratio of the amount of the element of interest in the sample to that in the final Pu fraction) were all above  $10^5$  for U, Th and Am. The recovery of Pu ranged from 72% to 92% for certified reference materials of sediment. The overall sample separation for one run can be carried out within one day. Momoshima et al. [51] also used TEVA to separate Pu in soils and sediments. Sample loading was carried out in 2  $\text{mol L}^{-1}$   $\text{HNO}_3$  followed by washing with 8  $\text{mol L}^{-1}$   $\text{HNO}_3$  and 6  $\text{mol L}^{-1}$  HCl. Pu was eluted with a diluted acid solution, namely, 0.5  $\text{mol L}^{-1}$  HCl.

TRU is another extraction chromatographic resin often used for the separation of actinides in  $\text{HNO}_3$  or HCl media [84]. As opposed to TEVA, TRU contains octyl (phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide dissolved in tri-n-butyl phosphate. TRU has been utilized for a vast number of analytical purposes, including separation of the actinides as a group from the sample matrix; group actinide separation based on the valence state and individual separation of Am/Cm and Pu from each other. Actinides in III, IV and VI oxidation states are strongly retained by TRU in  $>0.5 \text{ mol L}^{-1}$   $\text{HNO}_3$ , while most of matrix constituents and potentially interfering radionuclides are not. Am and radionuclides in trivalent oxidation state, which are not retained by TRU resin in HCl medium, can be eluted from the column with 4–6  $\text{mol L}^{-1}$  HCl, whereas tetravalent and hexavalent actinides are strongly retained. Pu is finally selectively eluted by on-column reduction of Pu to Pu(III), which is not retained in hydrochloric acid medium. Hence, the other actinides such as U, Th, Np still remain on the column. For instance, Kaye et al. [85] performed the separation of Pu in soil, tank sludge and waste samples by TRU resin using ascorbic acid to reduce iron to Fe(II) in order to prevent the uptake of Fe(III). The sample was loaded in 2  $\text{mol L}^{-1}$   $\text{HNO}_3$ , followed by 2  $\text{mol L}^{-1}$   $\text{HNO}_3$ –NaNO<sub>2</sub>(s) to retain Pu as Pu(IV). Pu was finally isolated by

elution with 0.1  $\text{mol L}^{-1}$  hydroquinone–4  $\text{mol L}^{-1}$  HCl after washing Am and Cm off with 4  $\text{mol L}^{-1}$  HCl.

### 3.3.2. Coupling of extraction columns

UTEVA, composed of diantylmethylphosphonate sorbed on an inert polymeric support, is usually used for the pre-concentration and separation of uranium in  $\text{HNO}_3$  or HCl media [86]. In a number of radiochemical procedures, UTEVA resin has been employed in combination with TRU resin [62] and other resins. Toribio et al. [65], for example, devised an extraction chromatographic method for separation of Pu in soils and sediments by coupling UTEVA and TRU resins in tandem to improve the separation efficiency. In this procedure,  $\text{Fe}(\text{NH}_2\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$  and ascorbic acid were used to reduce Pu to Pu(III). The sample in 3  $\text{mol L}^{-1}$   $\text{HNO}_3$  was passed through the UTEVA resin and delivered to the TRU column. Pu in trivalent state, which should not be sorbed on UTEVA, was loaded on TRU, while U(VI) and Th(IV) were efficiently sorbed on UTEVA column and therefore removed. Pu on the TRU resin was oxidized to Pu(IV) by 2  $\text{mol L}^{-1}$   $\text{HNO}_3$ –0.1  $\text{mol L}^{-1}$  NaNO<sub>2</sub> in order to wash Am(III) by column rinsing with  $\geq 4 \text{ mol L}^{-1}$  HCl. Pu was finally eluted after reduction by a 0.1  $\text{mol L}^{-1}$   $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution. The average recovery of Pu was better than 80%. Varga et al. [54] employed a similar procedure to separate Pu in sediments and soils. In this case, Pu in 4  $\text{mol L}^{-1}$   $\text{HNO}_3$  was reduced to Pu(III) by  $\text{NH}_2\text{OH} \cdot \text{HCl}$ . Similar Pu yields as those of Toribio et al. [65] were obtained.

Mellado et al. [61] compared three separation methods for the determination of Pu, Am, Th and Sr in sediment samples. In the first method, four chromatographic extraction columns were used including two TRU columns, one UTEVA column and one Sr column as well. After addition of NaNO<sub>2</sub>(s), the sample in 4  $\text{mol L}^{-1}$   $\text{HNO}_3$  was loaded onto the first TRU resin, followed by a washing step with 3  $\text{mol L}^{-1}$   $\text{HNO}_3$  to remove Sr along with Ca, Al, Na, K. The remainder of the method involving the UTEVA/TRU tandem has been explained earlier in this section. This method yielded rather low recoveries of Pu, viz.,  $41.2 \pm 19.0\%$ , for a standard reference material. The second method was almost the same as the first procedure, with the exception of the addition of ascorbic acid to the original sample before loading onto the TRU column to reduce Fe(III) interfering effects. Pu recoveries for the reference material were now increased to  $84 \pm 6\%$ . In the third method, the first TRU column was removed. The UTEVA column was connected onto the top of TRU and in turn onto Sr column. Ascorbic acid was also used to reduce Fe(III) to Fe(II). The recoveries of Pu for reference material were now  $56 \pm 8\%$ . As seen from the above results, relatively high Pu recoveries were obtained with the second separation process. The low recoveries of Pu in the first method were attributed to the competitive adsorption of Fe(III) onto the TRU column. With the removal of the first TRU column, matrix ingredients were proven to interfere severely with Pu isolation using the tandem UTEVA/TRU resins.

## 3.4. High performance liquid chromatography

High performance liquid chromatography (HPLC)-based methods can be regarded as an appealing alternative to low to medium pressure extraction chromatography for efficient separation of actinides in complex environmental samples. In this context, the work by Perna et al. [63] is worth mentioning. The authors described a procedure for the simultaneous separation and determination of lanthanides and actinides (viz., Pu, Np, U, Am and Cm) from spent nuclear fuel samples and sediment standard reference material based on the usage of a mixed-bed anionic/cationic chromatographic column (CS5A, Dionex). Different redox reagents in acid media were tested for converting Pu and Np into appropriate oxidation states. It was demonstrated that among  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ , NaNO<sub>2</sub>, Ag<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub> and  $\text{NH}_2\text{OH} \cdot \text{HCl}$ , only H<sub>2</sub>O<sub>2</sub> and NaNO<sub>2</sub> were

able to transform both Pu and Np in the samples into tetravalent forms. The retention times of Np and Pu were far from U, whereby the potential interferences in samples with high uranium content are overcome. Detection limits of  $0.25 \text{ ng mL}^{-1}$  and  $0.45 \text{ ng mL}^{-1}$  were obtained for lanthanides and actinides, respectively, using ICP-MS as a hyphenated detection system. Analytical precision was typically better than 5%.

Truscott et al. [64] exploited high-performance chelation ion chromatography and detection by sector-field (SF)-ICP-MS, using polystyrene-divinylbenzene loaded with 0.1 mM dipicolinic acid for the separation of actinides, including Pu, in reference soil materials. In particular,  $^{238}\text{U}$  was separated from  $^{239}\text{Pu}$  to overcome the serious isobaric interference of  $^{238}\text{U}^1\text{H}^+$  and tailing of  $^{238}\text{U}$  on  $^{239}\text{Pu}$ . The studies on the oxidation states of the ions indicated that Pu(III) eluted near the solvent front, while Pu(IV) eluted much later and after U(VI). The detection limit for  $^{239}\text{Pu}$  was 8 fg for a 0.5 mL injection.

### 3.5. Combination of different chemical separation methods

Several researchers hyphenated various separation methods based on different chemical interactions aimed at improving the decontamination factors for potential interfering elements on Pu determination as detailed in this section with selected representative examples. For instance, Donard et al. [58] proposed an analytical procedure for simultaneous determination of  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{241}\text{Pu}$  and  $^{242}\text{Pu}$  in marine sediments using a combination of ion exchange chromatography and solvent extraction. Within this work, a Bio-Rad AG  $1 \times 8$  anion exchange resin was used in the primary separation stage to separate plutonium from sample matrix components, followed by solvent extraction with TTA-xylene for further separation of Pu from interferences, such as Am but mostly U. A second anion exchange resin, Dowex  $1 \times 8$ , was used for final purification of Pu. The analytical sequence is characterized by a reproducible yield of 42% Pu. Moreover,  $^{238}\text{U}$  and  $^{241}\text{Am}$  were both efficiently eliminated from the sample matrix. However, this procedure is somewhat time-consuming and labour intensive.

Jernstrom et al. [87] proposed a separation procedure for Am(III) and Pu(III) based on the coupling of TEVA extraction chromatography and mixed bed ion chromatography with quaternary ammonium and sulfonic acid exchange groups. Pu was firstly reduced to Pu(III) with ascorbic acid and  $\text{NH}_2\text{OH}\cdot\text{HCl}$ . The separation of Pu(III) and Am(III) from lanthanides was performed with TEVA in ammonium thiocyanate-formic acid media, whereupon Pu(III) and Am(III) were pre-concentrated onto the ion-exchanger prior to the final multi-modal chromatographic separation.

Separation of Pu in soils and sediments was also accomplished using a combination of TRU extraction chromatography and anion exchange separation [48]. The anion exchange resin was used for further purification of Pu by removal of concomitantly eluted U from TRU resin. The recovery of Pu was typically close to 60%, and decontamination factors for U and Th ranged from  $10^3$  to  $10^4$ . In this context, the work by Kim et al. [57] exploiting the chelating Diphonix resin (Eichrom) to separate U, Pu, Th, Am in environmental solids should also be mentioned. Actinides were eluted with  $0.5 \text{ mol L}^{-1}$  HEDPA, and the complexes in the eluate were decomposed by ozonation or usage of Fenton's reagent to release actinides. The separation of Pu from other elements (Am, U, and Th) was performed on a TRU resin. Chemical recoveries of  $85 \pm 5\%$  for Pu were in this case obtained. Tavcar et al. [55] developed a method for simultaneous separation of Pu and other radionuclides (Am, Np, and Sr) in soil and sediments by the combination of anion exchange separation and extraction chromatography (TRU-Spec and Sr-Spec) with averaged chemical recoveries of 61%.  $\text{NH}_2\text{OH}\cdot\text{HCl}$  and  $\text{NaNO}_2$

were employed to adjust Pu to Pu(IV) before loading on the anion exchanger for retention of Pu on the column as  $\text{Pu}(\text{NO}_3)_6^{2-}$ . Separation of Am and Sr were performed using the TRU-Spec and Sr-Spec sorbents, respectively.

However, for samples of limited amount, the possibility of performing sequential analysis of a series of analytes (e.g., Pu, Np, Am, Th, Po and U) might be troublesome and demands for complicated designs of analytical procedures.

### 3.6. Comparison of different chemical separation methods

To date, only a few investigations have been devoted to the comparison of different chemical separation methods for Pu [88]. When comparing anion-exchange separation using, e.g., Dowex  $1 \times 8$  with extraction chromatography with TEVA resin, decontamination factors for U are in both resins in the order of  $10^4$ – $10^5$  [88]. Chemical yields for Pu are within the interval of 54–99% and 46–80% for Dowex  $1 \times 8$  and TEVA, respectively, depending on the operation conditions. However, the TEVA-extraction chromatographic method features lower acid consumption and gives rise to higher decontamination factors for Fe, Mn and Ce.

As regards the comparison of chemical separation using either a single anion-exchanger (Dowex  $1 \times 8$ ) or two extraction chromatographic columns (e.g., UTEVA and TRU) [82], Pu recoveries are normally better for ion exchange rather than extraction chromatographic separations (60% vs 42%). This can be explained by the fact that one column is merely needed in ion exchange separation as compared to the extraction chromatographic method which usually requires the hyphenation of two extraction columns in series for accurate determinations.

## 4. Source preparation

Source preparation is a crucial step in radiochemical analysis. Generally sources for alpha spectrometric measurement of environmental samples are prepared by electro-deposition or electroplating [47,48,54,62,67], or co-precipitation/micro-precipitation [45,50,51,55,56,65,89]. Normally,  $\alpha$ -source of Pu is prepared by electro-deposition onto a stainless disk in an oxalate or sulphate medium. Pu is electrodeposited under a direct current ( $300$ – $400 \text{ mA/cm}^2$ ) for 2–4 h. Several drops of ammonia are needed to be added to the cell before disconnecting the current in order to stabilize the Pu precipitate on the disk. Detection of Pu on disks after electrodeposition might be also performed by laser-ablation (LA)-ICP-MS [47]. For the source preparation using co-precipitation, fluorides ( $\text{NdF}_3$ ,  $\text{LaF}_3$ , and  $\text{CeF}_3$ ) or iron hydroxides, as mentioned in the sample pre-treatment step, have been employed. However, this method is not widely used any longer because of the potential losses of Pu and deteriorated spectra resolution during the  $\alpha$ -spectrometry measurement. In fact, Pilvio and Bickel [90] proved that co-precipitation cannot yield as high Pu recoveries as that of electrodeposition. If Pu is measured by mass spectrometric techniques the final solution is preferentially prepared in weak  $\text{HNO}_3$  (around  $0.5 \text{ mol L}^{-1}$ ) medium.

## 5. Detection of Pu isotopes

There are two types of detection techniques for determination of Pu: (i) radiometric techniques including  $\alpha$ -spectrometry, gamma/X-ray spectrometry and liquid scintillation counting (LSC), in which Pu is measured by its radioactive decay; and (ii) mass spectrometric techniques where the atoms of individual Pu isotopes are detected on basis of their respective masses [91].

## 5.1. Radiometric method

### 5.1.1. $\alpha$ -Spectrometry

$\alpha$ -Spectrometry, as a traditional radiometric counting method, still plays an important role in the detection of Pu isotopes [45,56,71]. There are several types of detectors that can be used for the measurement of alpha emitting radionuclides, such as Frisch grid ionization chambers, proportional counters, plastic and liquid scintillation detectors and semiconductor detectors. Semiconductor  $\alpha$ -spectrometry, using a surface barrier or ion-implanted silicon detector, has been widely adopted as a powerful technique because of simplicity of measurement, good spectra resolution and reasonable sensitivity for specific radionuclides, especially those with short half-lives [92]. The energy resolution given as full width at half peak maximum ranges normally from 15 to 55 keV. A typical detection limit by  $\alpha$ -spectrometry is in order of  $10^{-4}$  Bq, which corresponds to about 0.05 pg of  $^{239}\text{Pu}$ .

Although  $\alpha$ -spectrometry has the advantages of easy application and relatively low instrument expenses, this detection technique requires very long counting times (1–30 days). Consequently,  $\alpha$ -spectrometric detection is not suitable for emergency situations, where analytical results should be obtained in a shorter time frame (<1 day). Further, the high charge and relatively low speed of alpha particles result in significant energy losses, even in very thin absorbers. Even though the energy losses in the source usually are not high enough to significantly lower the counting efficiency, the spectra becomes degraded with reduced resolution and increased peak overlapping. It is therefore imperative to completely separate Pu from all other elements in the sample matrix prior to alpha spectrometric detection.

$\alpha$ -Spectrometry is incapable of distinguishing between  $^{239}\text{Pu}/^{240}\text{Pu}$  and  $^{238}\text{Pu}/^{241}\text{Am}$  because of the limited energy resolution of alpha detectors. High-resolution  $\alpha$ -spectrometry in combination with spectral deconvolution is a useful method in resolving the  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  isotopes, but it requires spectra with good counting statistics. In addition,  $\alpha$ -spectrometric detection of long-lived  $^{242}\text{Pu}$  and  $^{244}\text{Pu}$  isotopes in environmental samples cannot be accurately performed due to their ultra-trace level concentrations and the low specific activity of these isotopes. It should be also borne in mind that  $^{241}\text{Pu}$  as a beta emitter is not detectable by  $\alpha$ -spectrometry [91]. There are however still several advantages with  $\alpha$ -spectrometry as compared to alternative techniques. The radiometric technique is very robust and reliable with a near 100% functional up-time, which should be kept in mind when comparing with e.g., mass-spectrometry. Spectra are extremely simple, thereby minimising the risks of misinterpretation due to potential interfering peaks and presence of stable elements even though the preliminary chemical separation might be tedious and time-consuming for  $\alpha$ -spectrometry. There is no energy dependent efficiency and, compared to mass dependent efficiency in mass spectrometry, quantification is simply done by relating to the isotopic yield determinant. Detector background can be kept extremely low (less than 1 count per week in Pu-window) and be used for several years without deterioration of background or resolution. With respect to mass spectrometry one of the assets of  $\alpha$ -spectrometry is the possibility of detection of the relatively short-lived  $^{238}\text{Pu}$ .

### 5.1.2. Liquid scintillation counting

Liquid scintillation counting (LSC), because of its poor energy resolution, cannot compete with  $\alpha$ -spectrometry. Nowadays, with the improvement of LSC detectors, the discrimination between  $^{238}\text{Pu}$  and  $^{239+240}\text{Pu}$  is however feasible [93]. In contrast to  $\alpha$ -spectrometry, LSC has proved useful for the determination of the soft beta-emitter  $^{241}\text{Pu}$  [93]. To this point, the stripping of  $^{241}\text{Pu}$  out from the source is not needed, therefore, discs can be retrieved again

for other purposes after LSC detection. But several problems have been described, e.g., if some contaminants (namely, Fe, Pt) are electroplated with Pu, quenching effects, which decrease the detection efficiency, shift of alpha and beta spectra and mis-classification of alpha/beta events might occur. Furthermore, the LSC results depend on the chemical recovery given by  $\alpha$ -spectrometry and the complicated efficiency calibration of the instrument.

## 5.2. Mass spectrometry

With conventional  $\alpha$ -spectrometry,  $^{238}\text{Pu}$  and the combined intensity of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  are usually measured while mass spectrometry facilitates the individual determination of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ . To identify the origin and total Pu-concentration is actually of great advantage to be able to determine both the  $^{239}\text{Pu}/^{240}\text{Pu}$  ratio as well as the  $^{238}\text{Pu}/^{239+240}\text{Pu}$  ratio. The two techniques thus complement each other. Mass spectrometry is an atom counting technique which overcomes some specific problems of traditional radiometric methods. So far, a vast number of mass spectrometric methods, including inductively coupled plasma mass spectrometry (ICP-MS) [94,46], thermal ionization mass spectrometry (TIMS), accelerator mass spectrometry (AMS) [95,96], resonance ionization mass spectrometry (RIMS) [67], secondary ion mass spectrometry (SIMS), and glow discharge mass spectrometry (GDMS) have been introduced to improve the sensitivity and detection limit of analytical methods for determination of Pu isotopes, e.g.,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ , in environmental samples as discussed in several review articles [91,97–100]. However, as a consequence of the low concentration levels of Pu in the environment, the short half-life of  $^{238}\text{Pu}$ , and relatively high concentration of  $^{238}\text{U}$ , the isobaric interference of  $^{238}\text{U}$  makes the unbiased detection of  $^{238}\text{Pu}$  in environmental samples unattainable by mass spectrometry, even with decontamination factors as high as  $10^8$  or better for U.

### 5.2.1. ICP-MS

ICP-MS is becoming more and more attractive for the determination of trace and ultra-trace level concentrations of Pu in environmental samples with advantages of high sensitivity, short analytical times, relatively easy operation, and multi-isotopic detection including beta-emitters and straightforward quantification using aqueous standard solutions [101]. The first reported attempt to determine  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  in environmental samples by ICP-MS was done in 1989 by Kim et al. [75]. However, in order to reduce the sample consumption and consequently minimize instrumental radioactivity contamination and reduce waste generation, high efficiency micronebulization might be combined with ICP-MS for precise and accurate determination of ultra trace radionuclides as well as their isotopic ratios. Various low-consumption nebulizers, such as the microconcentric nebulizer (MCN) [102,103], the high efficiency nebulizer (HEN) [104–109], the direct injection nebulizer (DIN) [110–112], oscillating capillary nebulizer (OCN) [113,114] and direct injection high efficiency nebulizer (DIHEN) [115–118] have been applied as effective sample introduction techniques in ICP spectrometers to increase introduction efficiency of analytes. The analytical characteristics of DIHEN for inductively coupled plasma quadrupole mass spectrometric (ICP-QMS) determination of trace level concentrations of long-lived radionuclides ( $^{226}\text{Ra}$ ,  $^{230}\text{Th}$ ,  $^{237}\text{Np}$ ,  $^{239}\text{Pu}$  and  $^{241}\text{Am}$ ) have been examined by Becker and co-workers and compared with those of cross-flow and MicroMist microconcentric nebulizers [116]. It was proven that DIHEN-ICPMS is the most suitable coupling for the sensitive and precise determination of long-lived radionuclides within the  $\text{ng L}^{-1}$  range.

Over the past decades, several types of ICP-MS including sector field (or high resolution) ICP-MS (SF-ICP-MS)



[45,54,58,59,64,72,89] and laser-ablation ICP-MS (LA-ICP-MS) [45,47,119] have been successfully applied to the determination of Pu in various matrices. SF-ICP-MS is one of the most appropriate detection instruments for isotopic analysis of Pu. As compared with ICP-QMS, SF-ICP-MS features improved resolution, thereby facilitating the minimization of spectral interferences, and high sensitivity at a low-resolution mode. Sturup et al. [59], for example, employed SF-ICP-MS for the determination of Pu isotopes and isotopes ratios in sediment and seawater. Detection limits of 5, 1, and 1 fg mL<sup>-1</sup> (11.5 μBq mL<sup>-1</sup>, 8.4 μBq mL<sup>-1</sup> and 3.8 mBq mL<sup>-1</sup>) were obtained for <sup>239</sup>Pu, <sup>240</sup>Pu and <sup>241</sup>Pu, respectively. Donard et al. [58] applied SF-ICP-MS for simultaneous detection of <sup>239</sup>Pu, <sup>240</sup>Pu, <sup>241</sup>Pu and <sup>242</sup>Pu in sediments. The measurement was carried out at a low-resolution mode ( $m/\Delta m = 400$ ), and two different detection procedures were used. In the first procedure, ten masses (from 235 to 244) were measured in order to screen the presence of <sup>243</sup>Am and <sup>236</sup>U as well as the signal intensity of <sup>238</sup>U for estimating the interference of <sup>238</sup>U in the detection of <sup>239</sup>Pu. In the second procedure, five masses (239, 240, 241, 242 and 244) were measured to quantify the activity of <sup>239</sup>Pu, <sup>240</sup>Pu, <sup>241</sup>Pu, <sup>242</sup>Pu as well as the tracer <sup>244</sup>Pu. Varga et al. [54] used SF-ICP-MS for monitoring <sup>239</sup>Pu, <sup>240</sup>Pu and <sup>241</sup>Pu in soils and sediments. The instrument was equipped with a single electron multiplier and the measurement was carried out at a low-resolution mode ( $m/\Delta m = 300$ ). The possible hydride and oxide interferences (e.g., <sup>238</sup>U<sup>1</sup>H<sup>+</sup> or <sup>207</sup>Pb<sup>16</sup>O<sub>2</sub><sup>+</sup>) were reduced using a desolvation sample introduction system. For further minimization of hydride formation in ICP-MS, sample desolvation was combined with Ar–N<sub>2</sub> mixed gas plasma. Although the addition of nitrogen might increase nitrogen containing polyatomic interferences, the UH<sup>+</sup>/U<sup>+</sup> ratio was lower than 10<sup>-5</sup>. Detection limits of 34 μBq g<sup>-1</sup>, 80 μBq g<sup>-1</sup>, and 54 mBq g<sup>-1</sup> for <sup>239</sup>Pu, <sup>240</sup>Pu and <sup>241</sup>Pu, respectively, were achieved. The same authors later reported improved detection limits of 21 μBq g<sup>-1</sup>, 14 μBq g<sup>-1</sup>, and 11.9 mBq g<sup>-1</sup> for <sup>239</sup>Pu, <sup>240</sup>Pu and <sup>241</sup>Pu, respectively, by using similar operation conditions for SF-ICP-MS but without application of Ar–N<sub>2</sub> mixed gas plasma [71]. However, the <sup>241</sup>Pu results had relatively large uncertainty if the intensity of signals is rather low. It is also worth to mention in this context the contribution of Schamloff et al. [72] because of the development of an analytical procedure based on nano-volume flow injection and SF-ICP-MS for the determination of Pu in tap water. Solution introduction into SF-ICP-MS was performed using a nano-volume injector with a microflow total consumption nebulizer. This nebulizer featured efficient sample introduction and analyte ionization, leading to improved method sensitivity. An absolute detection limit of 150 fg <sup>242</sup>Pu using a 54 nL injection loop was reported.

LA-ICP-MS has the advantage of direct sampling of solid material surface without dissolution neither dilution of samples. Boulyga et al. [47] combined LA-ICP-MS with isotope dilution for the determination of Pu and Am in mosses after electrodeposition. Although the use of laser ablation did not eliminate UH<sup>+</sup> completely, the interfering effects were reduced significantly as a result of the generation of a dry aerosol [45,119]. A detection limit of 0.3 pg g<sup>-1</sup> for Pu isotopes was achieved by the combination of a modified laser ablation system providing high ablation rates and double-focusing SF-ICP-MS. Experimental results were in satisfactory agreement with certified values obtained with both α-spectrometry and ICP-MS after sample pre-treatment and chemical separation. However, inhomogeneous distribution of the analyte in the sample, in particular the presence of “hot” particles, might affect the precision and accuracy of the analysis.

Unfortunately, the accurate determination of Pu by ICP-MS is hampered by both spectral and non-spectral interferences. The major problem with spectral interferences is caused by the occurrence of isobars and polyatomic molecules in the plasma, of which

the most important are <sup>238</sup>U, <sup>238</sup>UH<sup>+</sup>, <sup>238</sup>UH<sub>2</sub><sup>+</sup> and <sup>241</sup>Am which overlap with the measurement of <sup>238</sup>Pu, <sup>239</sup>Pu, <sup>240</sup>Pu and <sup>241</sup>Pu isotopes, respectively. Thus, ICP-MS detection requires good separation of <sup>238</sup>U prior to <sup>239</sup>Pu determination and elimination of polyatomic chlorides and oxides. The tailing effect (low abundance sensitivity) from the high signal of <sup>238</sup>U is another drawback which limits the actual application of SF-ICP-MS. Moreover, the extremely low concentrations of Pu in the environment and high salt and organic matter content often lead to signal suppression, and consequently, to poor method accuracy.

### 5.2.2. AMS

AMS is among the most sensitive detection techniques for many long-lived radionuclides. Detection limits for <sup>239</sup>Pu are for example down to 10<sup>6</sup> atoms. Moreover, AMS features much lower matrix interfering effects compared to ICP-MS. For Pu isotopes, the main advantage of AMS with respect to conventional MS (TIMS or ICP-MS) is the complete destruction of molecular isobars (e.g., <sup>238</sup>UH<sup>+</sup> for <sup>239</sup>Pu) by stripping to highly positive charge states in the terminal of the tandem accelerator. Furthermore the abundance sensitivity is the best among the different mass-spectrometry techniques.

Fifield et al. [120] reported the first quantitative application of AMS to the determination of Pu isotopes in environmental samples at levels below those attainable with existing techniques (e.g., α-spectrometry and ICP-MS). In addition, determination of the <sup>240</sup>Pu/<sup>239</sup>Pu ratio is readily accomplishable. McAninch et al. [96] demonstrated that the installation of a heavy element spectrometer including a 45° cylindrical electrostatic analyzer is central to improve abundance sensitivity and minimize <sup>238</sup>U interference, hereby background levels are reduced to below 1 × 10<sup>6</sup> atoms per sample at masses 237, 239, 240 and 241 while allowing simplification of the sample preparation. Hrnccek et al. [56] determined Pu isotopes in nuclear weapons test sites and stressed that the AMS and α-spectrometric results were in good agreement. With the increasing number of AMS facilities, a large number of AMS applications have been devoted to the determination of Pu isotopes in environmental samples.

### 5.2.3. TIMS and RIMS

To some extent, TIMS has better sensitivity and precision for isotope ratio measurements than ICP-MS. TIMS with multiple ion collectors is generally the method of choice for isotope ratio measurements with high precision (down to 0.002%). Efurd et al. [121] conducted the analysis of soils and sediments using TIMS to determine the ratio of <sup>240</sup>Pu/<sup>239</sup>Pu. The spectrometer was equipped with a sample turret that held five surface ionization diffusion controlled filaments. Problems with spectral interferences of uranium in TIMS are less severe as uranium and Pu have different ionization potentials and thus are emitted from the filament at different temperatures. In addition, the introduction of dry samples reduces the formation of UH<sup>+</sup> species to a large extent. TIMS requires, however, an expensive instrument and robust separation to ensure the constant ionization of the analyte. This technique is also very time consuming, labour intensive and cannot be used for on-line detection because pre-concentration of Pu has to be done manually on a filament. Further, the mass-fractionation effect requires the determination of accurately known isotope ratio standards in order to be gain benefit from the high reproducibility of the instrument.

RIMS is well suited for trace analysis of long-lived Pu isotopes. In RIMS, the evaporated liquid samples on a filament are atomized by an atomic beam source. One or, in most cases, more lasers are tuned precisely to the wavelength required for the excitation and ionization of evaporated atoms in order to obtain a highly selective resonance ionization of the element of interest. RIMS is

highly sensitive because of the large atomic cross-section on the excitation–ionization process and the good detection efficiency. A detection limit of  $10^6$ – $10^7$  Pu atoms has been achieved for the overall isotopes, regardless of their half-lives and decay modes [67]. The high sensitivity of RIMS fosters the exploitation of a simplified procedure for the chemical preparation of samples as compared to the requirements of thin sources for  $\alpha$ -spectrometry. Gruning et al. [122] developed a pulsed RIMS apparatus with a neodymium-doped yttrium aluminium pumped titanium–sapphire laser system for detection of Pu isotopes. A detection limit of  $2 \times 10^6$  atoms was achieved. However, no commercial RIMS instruments are yet available.

### 5.3. Comparison of detection techniques

Table 7 summarizes the figures of merit of different detection techniques for Pu isotopes. For the determination of  $^{238}\text{Pu}$  and  $^{239+240}\text{Pu}$ ,  $\alpha$ -spectrometry is still a powerful technique because of simplicity of measurement, good resolution and reasonable sensitivity. In fact,  $\alpha$ -spectrometry is the only method suitable for detection of  $^{238}\text{Pu}$ . However, long counting times for low activity samples are needed and separation of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  is difficult. Detection of  $^{241}\text{Pu}$  by LSC features several advantages including fast analysis without need for stripping Pu out of the disc after determination of alpha emitters. Of the mass spectrometric methods, ICP-MS is commonly selected for simultaneous measurement of  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ , and sometimes  $^{241}\text{Pu}$ , in environmental samples. TIMS and AMS might provide improved sensitivity yet the analyses are costly. As to TIMS, the separation procedure is so critical that a preliminary extraction/chromatographic method should be repeated at least twice to separate Pu from matrix constituents. But the detection limit and precision of isotopic measurements are better in TIMS. AMS operation is more complex and a well experienced team is required. Yet, this detection technique is earning popularity because of instrumental developments. RIMS offers a number of assets as compared to other mass spectrometric techniques, including minimization of isobaric interferences, good detection limits, high selectivity and short detection times. However, the application of RIMS is still limited because a limited number of facilities are at disposal and the instruments are not currently commercially available. It should also be kept in mind that although advanced mass spectrometric techniques might be used for sensitive determination of plutonium isotopes relevant issues regarding plutonium behaviour and distribution in the environment could be tackled using simpler radiometric methods.

## 6. Automated determination of Pu isotopes

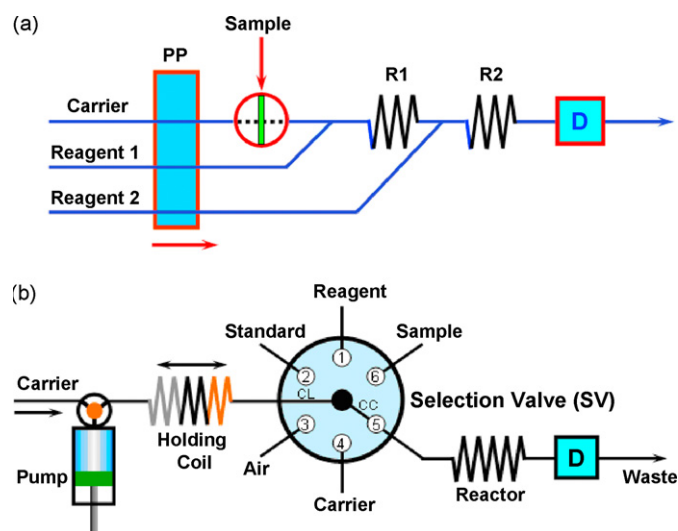
### 6.1. Principles of flow injection and sequential injection

Radiometric and MS determination of Pu in environmental samples requires as explained earlier some degree of separation of Pu from stable matrix and interfering radionuclides in order to obtain reliable analytical data. Therefore, radionuclide pre-concentration and separation methods remain to be an important and often critical part of the overall radioanalytical protocol. Many of the current analytical procedures for separating and determining Pu in complex samples are several decades old. Although sensitive, precise, and accurate, these classical procedures can often be time-consuming and labour intensive, based on use of corrosive or toxic chemicals, and leading to the generation of substantial amounts of secondary hazardous liquid and solid wastes. The main reasons for changing previous protocols are devoted to the need of their adaptation to mass spectrometric detection, which is in continuous growing, and also the expedition of the overall analysis procedure. The mech-

anization or automation of analytical systems for separation and determination of Pu should be regarded as an attractive avenue to accelerate support operations and decrease expenses in the characterization of wastes and monitoring of the environment as well. Flow injection (FI) analysis [33,35–37], and its second-generation so-called sequential injection (SI) analysis [39], represent attractive tools to automate various separation methods, such as solvent extraction and column separation prior to analyte (e.g., radionuclide) detection [41,42,44].

Flow injection analysis has found wide application as a non-chromatographic technique for automated quantitative analysis [125]. Exploiting chemical and/or physical kinetic control of the analytical method, the selectivity and speed of the analysis are often superior to those of conventional batchwise equilibrium counterparts [33,35]. The precise control of physical variables in an entirely enclosed system has been used to design powerful analytical systems for many applications, including environmental trace analysis [33–37]. Conditions that would normally foul or deteriorate the detector can be automatically and systematically overcome by using FI approaches. A schematic illustration of a three-line flow injection system is presented in Fig. 3(a) and consists of a peristaltic pump (PP) that is used to propel the carrier stream through a narrow tube (0.3–0.8 mm i.d.); an injection device that introduces a minute, well-defined volume of sample solution (typically  $\geq 25 \mu\text{L}$ ) into the carrier stream in a very reproducible manner; reaction coil(s) (R1 and R2) in which the sample zone disperses and reacts with the reagent(s), forming species that are detected by a flow-through detector (D); which records the transient FI readouts.

As a result of growing environmental demands for reduced consumption of sample and reagent solutions, the first generation of FI, which utilizes continuous pumping of carrier and reagent(s), was in 1990 supplemented by SI [126]. Sequential injection is based on using programmable, bi-directional discontinuous flow as precisely coordinated and controlled by a computer. The SI analyzers can be configured to perform most operations of conventional FI, with no or minimal physical reconfigurations of the manifold when aiming at multiparametric assays [35,39]. A sketch of a typical SI-manifold is reproduced in Fig. 3(b). The core of the system is a multi-position selection valve (here shown as a 6-port valve), furnished with a central rotary communication channel (CC) that can be made to address each of the peripheral ports (1–6), and a central communication line (CL) which, via a holding coil (HC), is connected to a syringe pump



**Fig. 3.** Diagram of a three-line FI system (a) and an SI set-up furnished with a syringe pump (b) PP: peristaltic pump; R1: reaction coil 1; R2: reaction coil 2; D: detector. (Adapted from Ref. [40] with permission from Elsevier.)

operating as the liquid driver. By directing the central communication channel to the individual ports, well-defined and precisely metered sample and reagent zones (typically 5–25  $\mu\text{L}$ ) are initially aspirated sequentially into the holding coil where they are stacked one after the other. The holding coil prevents the aspirated solutions from entering into the pump. Afterwards, the selection valve is switched to the outlet port (here position 5), and the segments are propelled forward towards the detector, undergoing on their way dispersion and thereby partial mixing with each other, and hence promoting chemical reaction, the result of which is monitored by the detector.

The main assets of automated SI methods in comparison to the traditional separation methods for radionuclides [127] include: (i) improved practitioner safety because manual operations are scarcely needed and the separation is performed in a fully enclosed system; (ii) rapid execution of sample processing steps; (iii) on-line hyphenation to the detector, e.g., ICP-MS or LSC; (iv) decreased reagent consumption and radioactive waste generation; (v) less sample cross-contamination by appropriate execution of clean-up steps; and (vi) high recovery, good selectivity and acceptable reproducibility. The instrumental simplicity, flexibility, robustness, minimal operational maintenance and ease with which hydrodynamic variables can be controlled in SI, have turned it into a very appealing choice within both research and to some extent to industrial laboratories for automation of chemical assays.

## 6.2. FI/SI-based separations for on-line determination of Pu

FI/SI assemblies have been over the past few years devised for on-line analysis of environmental samples contaminated with Pu. Relevant analytical procedures for automatic determination of Pu in different environmental matrices are summarized in Table 9 and described in the following subsections. Based on the type of the resins utilized in the separation procedure, on-line FI/SI column separation systems can be divided into two categories, i.e. those involving extraction chromatography and those based on the use of ion exchange chromatography.

### 6.2.1. FI/SI-based extraction chromatographic separations

**6.2.1.1. Single column.** The first reported application of FI/SI for determination of Pu was developed by Egorov et al. [128] based on a methodology introduced by Horwitz et al. [83]. The developed FI procedure focused on the separation of Am and Pu from

each other and from interfering matrix constituents (e.g., fission products) using the actinide-specific TRU-resin column. The separation of Am and Pu was performed by sample uptake in a 1 mol L<sup>-1</sup> HNO<sub>3</sub> medium, in which Pu was adjusted to Pu(III), wash of the column with 1 mol L<sup>-1</sup> HNO<sub>3</sub> to remove matrix and interfering radionuclides, adjustment of Pu valence to Pu(IV) with 0.5 mol L<sup>-1</sup> NaNO<sub>2</sub>–2 mol L<sup>-1</sup> HNO<sub>3</sub>, elution of Am(III) with 4 mol L<sup>-1</sup> HCl, and then selective recovery of Pu by reduction to Pu(III) with 0.02 mol L<sup>-1</sup> TiCl<sub>3</sub>–4 mol L<sup>-1</sup> HCl following a similar analytical method as described above in Section 3.3. Radiometric detection was performed on-line using a flow-through liquid scintillation detector. Fajardo et al. [129] reported an automated system for the separation of Pu and Am using this separation procedure and multisyringe flow injection analysis–multipumping flow system. Grate and Egorov [130] further investigated and optimized the above-mentioned FI system for separation of Am and Pu. Selective Pu elution using different reducing agents was studied and the effects of column size, and flow rate were discussed as well. It was found that 0.1 mol L<sup>-1</sup> hydroquinone, 0.2 mol L<sup>-1</sup> semicarbazide, 0.2 mol L<sup>-1</sup> ascorbic acid, 0.05 mol L<sup>-1</sup> SnCl<sub>2</sub> and 0.2 mol L<sup>-1</sup> NaI in 4 mol L<sup>-1</sup> HCl solution proceeded slowly and resulted in wide and severely tailed elution profiles. On the other hand, reduction with 0.05 mol L<sup>-1</sup> (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>–0.1 mol L<sup>-1</sup> ascorbic acid and 0.02 mol L<sup>-1</sup> TiCl<sub>3</sub> gave sharp and complete Pu elution without significant tailing. Experimental results revealed that the on-line TiCl<sub>3</sub>-based elution performed more reliably as compared to (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>–ascorbic acid elution when the separation was carried out on larger columns. The results of the flow-through extraction chromatographic method using standard Pu and Am solutions indicate that Am–Pu separation can be performed rapidly (<10 min) and recoveries of Pu and Am were quantitative (around 100%). Grate et al. [131] also reported an SI separation system for determination of Pu, Am, Cm and Th from nuclear waste samples using TRU-based extraction chromatography. On-line LSC was used to detect eluted species during method development, and fraction collection and  $\alpha$ -spectroscopy were used for quantification. Selective separation of Pu was achieved via on-column redox reactions. In this approach, all of the Pu was adjusted in a single oxidation state of Pu(III) with the addition of solid sulfamic acid and ascorbic acid before sample loading. To perform on-column Pu oxidation, an oxidizing agent (NaNO<sub>2</sub>) was included in the column washing step, followed by elution of trivalent actinides with 4 mol L<sup>-1</sup> HCl. Pu(VI) retained on the column is then reduced and eluted as Pu(III)

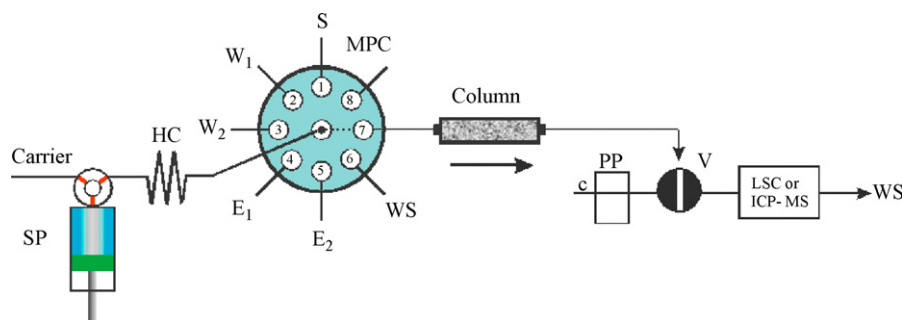
**Table 9**

Comparison of different analytical procedures for automatic determination of Pu exploiting flow-based approaches.

Sample	Separation method	Decontamination factor of <sup>238</sup> U	Recovery of Pu	Detection technique	Nuclide	Detection limit	Operation time	Ref.
Synthetic solution	FI-TRU	–	–	LSC	<sup>239</sup> Pu	–	–	[128]
Synthetic solution	FI-TRU	–	98–100%	LSC	<sup>239</sup> Pu	–	10 min	[130]
Nuclear waste	SI-TRU	–	85%	LSC and $\alpha$ -spectrometry	<sup>238</sup> Pu <sup>239+240</sup> Pu	–	–	[131]
Nuclear waste	SI-TRU	$3.0 \times 10^5$	–	ICP-MS	<sup>239</sup> Pu <sup>240</sup> Pu <sup>241</sup> Pu <sup>242</sup> Pu	–	–	[132]
Soil	SI-TRU	–	–	SF-ICP-MS	<sup>239</sup> Pu	1.9 $\mu\text{Bq}$	–	[124]
Soil or sediment	SI-Sr and TEVA	$10^4$ – $10^5$	>70%	SF-ICP-MS	<sup>239</sup> Pu <sup>240</sup> Pu <sup>242</sup> Pu	9.2 $\mu\text{Bq}$ 25 $\mu\text{Bq}$ 0.87 $\mu\text{Bq}$	5 h <sup>a</sup>	[135]
Seawater	SI-Sr and TEVA	$(1.6\text{--}3.8) \times 10^4$	>58%	SF-ICP-MS	<sup>239</sup> Pu <sup>240</sup> Pu	0.98 $\mu\text{Bq}$ 1.04 $\mu\text{Bq}$	4 h	[136]
Soil, sediment	SI-TEVA	$8.8 \times 10^5$	87–95%	SF-ICP-MS	<sup>239</sup> Pu <sup>240</sup> Pu	– –	1 h	[133]
Soil	SI-Dowex 1 $\times$ 8	–	85–96%	$\alpha$ -Spectrometry	<sup>239+240</sup> Pu	–	5.23 h	[137]
Leaves	FI-AG MP-1M	–	>85%	ICP-DRC-MS	<sup>239</sup> Pu <sup>240</sup> Pu <sup>241</sup> Pu <sup>244</sup> Pu	0.07 $\mu\text{Bq}$ 0.04 $\mu\text{Bq}$ 0.72 mBq 0.31 pBq	30 min	[138]

<sup>a</sup> Total analysis time.





**Fig. 4.** An SI manifold equipped with an extraction chromatographic column hyphenated to the analytical detection system via an ancillary FI manifold. SP: syringe pump; HC: holding coil 1; S: sample;  $E_1$ ,  $E_2$ : eluent 1, eluent 2;  $W_1$ ,  $W_2$ : washing solution 1, washing solution 2; WS: waste; MPV: multiport valve; PP: peristaltic pump; C: carrier; and V: valve. (Adapted from Ref. [42] with permission from Elsevier.)

using Fe(II)-sulfamate/ascorbic acid as the eluent. Experimental results in three types of aged nuclear waste reference materials including aged irradiated nuclear fuel, tank waste supernatant and vitrified nuclear waste were in good agreement with the certified values. The recovery of Pu was 85%. Using a similar manifold, the same group [132] combined SI with extraction chromatography on TRU resin and on-line ICP-MS detection for separation and determination of Am, Pu and Np in dissolved vitrified nuclear wastes. Reductive sample treatment procedures were used to adjust Pu and Np redox states prior to analysis. Uranium decontamination factors ranged from  $4.9 \times 10^3$  to  $3.0 \times 10^5$  when using Fe-ascorbic acid and Fe(II) sulfamate-based sample treatment, respectively. An SI manifold furnished with an extraction chromatographic column prior to the detection instrument is illustrated in Fig. 4.

Truscott et al. [124] developed an automated extraction chromatographic method using TRU resin in hyphenation with SF-ICP-MS for determination of Pu, Np, Th, U and Am in reference materials. Efficient elution of analytes from the mini column was proven feasible with small eluent volumes, thereby facilitating the on-line connection of the flow system to ICP-MS. The procedure however rendered low concentration for Pu in NIST 4353 (Rock Flats Soil), that is,  $2423 \pm 137 \text{ fg g}^{-1}$  versus the certified  $3307 \pm 248 \text{ fg g}^{-1}$ . A simultaneous analytical method for determination of  $^{237}\text{Np}$ ,  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  in soils was proposed by Kim and co-workers [133] using an SI system with TEVA-based sample separation coupled to SF-ICP-MS detection. TEVA resin maintained its re-usability for up to nine replicates, giving rise to high and consistent chemical recoveries (>90%), good selectivity for Pu and low analyte carryover. With the exception of the preparation process required prior to sample loading, the overall chemical purification sequence and detection by SF-ICP-MS could be completed within 1 hour. Recently, Epov et al. [134] developed a rapid on-line analytical method for the determination of Pu isotopes in soils and sediments. Flow injection chromatography using TEVA was exploited to separate and pre-concentrate Pu from other matrix constituents using ascorbic acid as a redox reagent. Pu was finally eluted with  $0.02 \text{ mol L}^{-1}$  HCl and detected by ICP-QMS using an APEX desolvation unit with a Mira Mist nebulizer to minimize clogging and hydride interferences. The total time for the on-line analysis of a single sample was about 23 min.

**6.2.1.2. Combination of extraction columns.** Kim and co-workers [135] reported an on-line separation method for pre-concentration of Pu and elimination of  $^{238}\text{U}$  with the use of isotope dilution-SF-ICP-MS for determination of ultra low level concentrations of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  in small amounts of soil and sediment. Two mini columns ( $4.6 \text{ mm i.d.} \times 30 \text{ mm}$  long PEEK column and  $3.0 \text{ mm i.d.} \times 25 \text{ mm}$  long borosilicate column) were assembled in series in the flow manifold. The first column packed with Sr resin was used to remove several interfering elements, including  $^{238}\text{U}$ , either quantitatively

or partially from the sample matrix. Pu was retained strongly on the Sr-resin in  $4 \text{ mol L}^{-1}$   $\text{HNO}_3$  and eluted with  $<1 \text{ mol L}^{-1}$   $\text{HNO}_3$ , whereas  $^{238}\text{U}$  was retained very weakly in  $<4 \text{ mol L}^{-1}$   $\text{HNO}_3$ . The second column packed with TEVA resin was used for further purification of Pu from other elements and decreasing the final eluate volume without increasing the concentration of concomitant  $^{238}\text{U}$ . The eluate of Sr resin containing Pu in  $0.8 \text{ mol L}^{-1}$   $\text{HNO}_3$  could be loaded onto TEVA resin directly because Pu was retained strongly in  $\geq 0.8 \text{ mol L}^{-1}$   $\text{HNO}_3$ , whereas  $^{238}\text{U}$  was retained weakly in  $\text{HNO}_3$  on the TEVA resin. Pu recoveries were over 70% and the final decontamination factors for  $^{238}\text{U}$  were in the order of  $10^4$ – $10^5$ . It was reported that the separation and detection of Pu in 1 g of soil or sediment could be achieved within about 5 h. The results obtained in this work were in good agreement with certified values with deviations of <10%. The detection limits for  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{242}\text{Pu}$  in a 2.4 mL final solution were 9.2  $\mu\text{Bq}$ , 25  $\mu\text{Bq}$ , 0.87  $\mu\text{Bq}$ , respectively. The same authors proposed a modification of the above FI system to make it suited for determination of Pu in seawater [136]. The chemical purification and pre-concentration of Pu isotopes were still performed by the application of two mini-columns ( $6.6 \text{ mm i.d.} \times 25 \text{ mm}$  long borosilicate column and  $1.8 \text{ mm i.d.} \times 20 \text{ mm}$  long PEEK column) of extraction resins, Sr and TEVA, respectively. But contrary to the previous study, the first column was enlarged to eliminate the large amount of Pb in seawater while the dead volume of the second column was 3-fold shortened to obtain narrow and sharp elution profiles. With this configuration, the detection limits for  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  in 650  $\mu\text{L}$  final eluate were 1.5  $\mu\text{Bq mL}^{-1}$  and 1.6  $\mu\text{Bq mL}^{-1}$ , respectively. The separation and measurement of Pu in 5 L seawater can be achieved within 4 h. The recoveries were ca. 58% and ten multiple analysis of certified reference seawater (IAEA-381) could be done without replacement of resins. The ranges of decontamination factors for U and Pb in 5 L of seawater were  $1.2$ – $2.4 \times 10^6$  and  $1.6$ – $3.8 \times 10^4$ , respectively.

#### 6.2.2. FI/SI-based ion exchange chromatographic separations

Kim and co-workers demonstrated the applicability of flow-through anion-exchange chromatography (e.g., Dowex  $1 \times 8$ ) for the separation and concentration of Pu in soils [137]. In this method,  $\text{NaNO}_2$  was used to adjust the Pu valence to Pu(IV) prior to sample loading. A series of solutions, viz.,  $8 \text{ mol L}^{-1}$   $\text{HNO}_3$ ,  $10 \text{ mol L}^{-1}$  HCl and  $0.1 \text{ mol L}^{-1}$   $\text{NH}_4\text{I} + 9 \text{ mol L}^{-1}$  HCl, were consecutively delivered to the anion-exchange column following sample loading for removal of uranium, americium and thorium, and elution of Pu, respectively. The total time for one run separation process was 5.2 h and two samples could be analyzed simultaneously within the designed flow system. The chemical recovery of Pu in the automated system ranged from 85% to 96% with a relatively low standard deviation of 8%.

A protocol for the determination of Pu in apple leaves (NIST 1515) has been reported by Epov et al. [138]. The method con-

sisted of microwave assisted digestion, flow injection on-line pre-concentration and matrix separation, and sample desolvation prior to introduction into ICP-dynamic reaction cell-MS. To investigate the separation of Pu from Fe and rare earth elements, three kinds of resins, i.e. one extraction resin (TRU) and two anion exchange resins (AG 1 × 8 and AG MP-1M) were investigated and compared with each other. It was found that both Fe and rare earth elements were not retained on AG 1 × 8 and AG MP-1M resins in HNO<sub>3</sub> medium, but sorbed on the TRU extraction resin and competed with Pu for sorption. Compared with TRU and AG 1 × 8 resins, AG MP-1M resin performed better affinity for Pu and thus AG MP-1M was recommended for Pu pre-concentration and sample clean-up in plant samples.

On-line coupling of ion-exchange separation with ICP-MS is however not a simple task because of the relatively larger volume of eluent required as compared to extraction chromatography and the incompatibility of common Pu eluents, typically a mixture solution of HCl with HI or NH<sub>4</sub>I, with the detector. Therefore, FI/SI based ion exchange chromatography is frequently performed in an off-line detection fashion, which on the other hand, foster the automated separation of several samples at a time as described in the literature [137].

## 7. Conclusions and outlook

In this article, recent analytical methods reported in the literature for pre-treatment, purification and determination of Pu isotopes in environmental matrices are comprehensively reviewed and critically compared. As to processing of solid samples, drying, ashing and acid or alkali digestion and co-precipitation are routine procedures, yet filtration, evaporation and co-precipitation are most frequently used for liquid samples. Valence adjustment is a crucial step to warrant high recoveries in separation procedures. Ion exchange and extraction chromatography are the most widely utilized methods both in a manual or automatic fashion as discussed in the bulk text. Ion exchange methods are simple and might be performed unattended but offer limited selectivity. On the other hand, extraction chromatographic procedures are flexible, highly selective but with moderate sensitivity. Up to date,  $\alpha$ -spectrometry and ICP-MS are the common detection methods for Pu isotopes. Radiometric measurements using  $\alpha$ -spectrometers are easy and cost-effective, but relative high analyte concentration and long measurement times are needed for accurate quantification. Detection of <sup>238</sup>Pu and <sup>239+240</sup>Pu is feasible, but not <sup>239</sup>Pu and <sup>240</sup>Pu individually. On the contrary, ICP-MS is fast, highly sensitive and capable of providing the individual concentrations of <sup>239</sup>Pu and <sup>240</sup>Pu, yet determination of <sup>238</sup>Pu is hindered by the presence of even minute amounts of <sup>238</sup>U in the Pu fraction. For the determination of <sup>241</sup>Pu liquid scintillation counting could be a good choice. If the comprehensive characterization of the sample is necessary, the rational use of all methods might be called for.

Automatic flow-based solid phase extraction methods have been herein presented as potential substitutes of off-line procedures that are tedious and labour-intensive. Notable advantages of these systems include the improved analysis time, the mechanization of sample processing, the minimal contact of the analyst with hazardous radionuclides and the drastic reduction in the consumption of sample and chemical reagents, hence resulting in less waste production, which is of particular importance nowadays due to the increasing costs in the disposal of chemical wastes. The application of FI/SI for simplification of radiochemical assays is however limited to a few laboratories, and traditional batchwise methods are still commonplace. This might be consequence of the downscaling of the column separation procedure, which might be inappropriate for concentration of large volumes of samples (often tens to

hundreds of litres) for sensitive quantification of Pu at environmentally relevant levels. In other instances, the decontamination factors obtained on-line are not high enough for accurate analysis. The progressive degradation of the sorbent material with repetitive use and sample cross-contamination are other well-known limitations of FI/SI systems with permanent columns. However, this drawback can be elegantly overcome by exploitation of the 'bead injection' concept, where the sorptive surfaces are replaced automatically with fresh beads after each analytical run [139,140]. However, with the requirement of rapid assays of Pu for emergency purposes and the increased application of ICP-MS, the hyphenation of FI/SI column separation with ICP-MS is expected to be exploited in the near future as a routine technique for environmental monitoring.

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## Paper II

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# Rapid isolation of plutonium in environmental solid samples using sequential injection anion exchange chromatography followed by detection with inductively coupled plasma mass spectrometry

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## ABSTRACT

This paper reports an automated analytical method for rapid determination of plutonium isotopes ( $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ ) in environmental solid extracts. Anion exchange chromatographic columns were incorporated in a sequential injection (SI) system to undertake the automated separation of plutonium from matrix and interfering elements. The analytical results most distinctly demonstrated that the crosslinkage of the anion exchanger is a key parameter controlling the separation efficiency. AG 1- $\times$ 4 type resin was selected as the most suitable sorbent material for analyte separation. Investigation of column size effect upon the separation efficiency revealed that small-sized (2 mL) columns sufficed to handle up to 50 g of environmental soil samples. Under the optimum conditions, chemical yields of plutonium exceeded 90% and the decontamination factors for uranium, thorium and lead ranged from  $10^3$  to  $10^4$ . The determination of plutonium isotopes in three standard/certified reference materials (IAEA-375 soil, IAEA-135 sediment and NIST-4359 seaweed) and two reference samples (Irish Sea sediment and Danish soil) revealed a good agreement with reference/certified values. The SI column-separation method is straightforward and less labor intensive as compared with batch-wise anion exchange chromatographic procedures. Besides, the automated method features low consumption of ion-exchanger and reagents for column washing and elution, with the consequent decrease in the generation of acidic waste, thus bearing green chemical credentials.

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## 1. Introduction

Plutonium has been released into the environment by nuclear activities, including nuclear weapon testing in the 1950ies–1980ies, reprocessing of spent nuclear fuel, accidents of nuclear power reactors and nuclear devices [1,2]. Plutonium is regarded as a highly radiological and biological toxic pollutant in the environment as a result of the relatively long half-lives of the most predominant isotopes ( $^{239}\text{Pu}$ : 24100yr;  $^{240}\text{Pu}$ : 6537yr) and the alpha emission associated with their decay [3]. Plutonium also exists in various radioactive wastes, and may potentially be released to the environment during storage and depository. Therefore, accurate quantification of Pu in diverse environmental samples is imperative in environmental risk assessment and radiological emergency preparedness as well as in nuclear waste treatment. High sample throughputs are also desirable in environmental monitoring and emergency situations to cope with

requirement of processing a large number of samples in a short time frame.

Over the past few decades, a wealth of analytical methods have been developed and applied to the determination of Pu, including co-precipitation, solvent extraction, anion exchange and extraction chromatography [4–15]. Of the various methods, anion exchange chromatography should be considered as a classical method given its widespread use in most of radio-analytical laboratories for routine determination of Pu in various environmental samples [9,12,16,17]. It offers the advantages of cost-effectiveness along with appropriate accuracy, sensitivity and repeatability in most radionuclide assays. However, the traditional anion exchange chromatographic procedure for separation of Pu from matrix elements and interfering nuclides is mostly operated in batch-wise manual fashion and therefore time consuming and labor intensive [1]. Besides, chromatographic columns with volumes of 10–20 mL are normally needed for the analysis of large-sized samples, for example, 10 g of soil, to be able to detect the target analytes at environmentally relevant concentrations. As a result, a large amount of acidic reagents for the removal of interfering elements and elution of Pu is usually required, which gives rise to the generation of a

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considerable volume of waste [12]. In some cases, a supplementary column is employed for further purification of Pu from uranium and other interferences, which makes the separation procedure cumbersome and inappropriate for screening protocols and emergency preparedness scenarios [18,19].

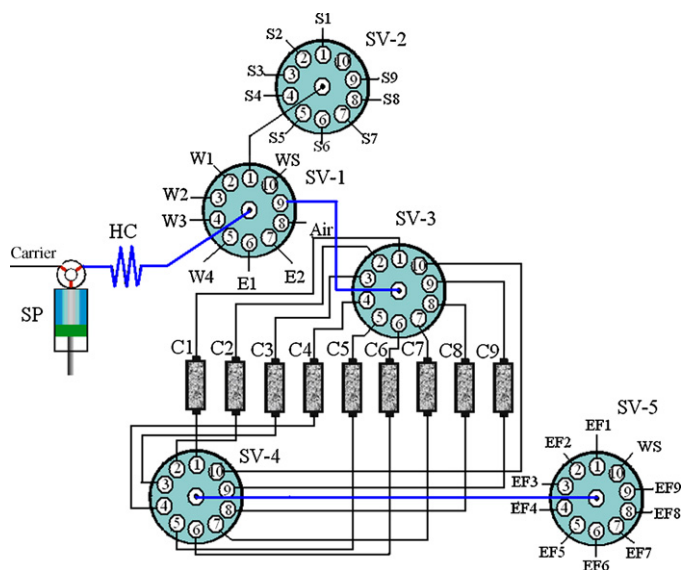
Flow injection (FI)/sequential injection (SI) approaches are regarded as appealing analytical tools for rapid and automated determination of low level of radionuclides in environmental samples, as pointed in a number of review articles [1,20–22]. There has been an increasing interest in the usage of FI and SI for Pu assays in diverse environmental and biological samples [23–25]. So far, most of the automated analytical methods reported in the literature resorted to extraction chromatographic procedures capitalized on Eichrom/TrisKem TEVA or TRU resins. To our best knowledge, only Kim et al. [26] reported an SI for determination of Pu in  $\leq 10$  g of soil using anion exchange chromatography, yet no FI/SI analytical method based on anion exchange chromatography has been reported to date for Pu determination in large-sized environmental samples. This might be due to the requisition of assembling flow networks with one or two large-bored anion exchange columns, which are not readily compatible with low-pressure FI/SI manifolds. Besides FI setups do not suffice flexibility to accommodate multi-stage analytical procedures as demanded in radionuclide separations [1,20–22].

Aiming at the automated determination of trace level concentrations of Pu in a large number of environmental samples with minimal operational maintenance, we propose in this work an SI anion exchange based manifold capitalized on user-friendly computer-controllable programming flow with detection by inductively coupled plasma mass spectrometry (ICP-MS). The influence of resin crosslinkage and particle size on the separation efficiency was investigated in detail to optimize the separation procedure and shorten the analytical times. Based on the investigation, a simple analytical method was developed and applied to the determination of trace level of Pu in environmental solids (namely, soils and sediments).

## 2. Experimental

### 2.1. Experimental setup

The automated flow-based setup is composed of an FIALab-3500B SI system (FIALab Instruments, Bellevue, WA) furnished with a syringe pump (SP, Cavo, Sunnyvale, CA, 25 mL capacity), an internal 10-port multi-position selection valve (SV-1), four external 10-port multi-position selection valves, SV-2–SV-5 (Valco Instruments, Houston, TX), and nine anion exchange columns (C1–C9) attached via ports 1–9 of SV-3 and SV-4, respectively. A schematic illustration of the SI-analyzer is given in Fig. 1. Within the system, nine samples can be sequentially separated in a fully computer controlled mode with the aid of the user-friendly FIALab associated software. All the outlets of the selection valve (SV-1) were connected through PEEK ferrules with rigid PTFE tubing (2.4 mm i.d./3.2 mm o.d.) and all the inlets and outlets of the external selection valves (SV-2–SV-5) were furnished with rigid PTFE tubing of smaller diameter (0.8 mm i.d./1.6 mm o.d.). The central port of the SV-1 was connected to the holding coil (HC), which consists of a 6.6-m-long PTFE tubing with an inner capacity of 30 mL (2.4 mm i.d./3.2 mm o.d.). Ports 10 of SV-3 and SV-4 were connected directly through a rigid PTFE tubing (0.8 mm i.d./1.6 mm o.d.) for the rinsing of the outlet tubing EF1–9. Hereby, it should be mentioned that two of the external selection valves, i.e., SV-2 and SV-5, could be replaced by an auto-sampler and eluate auto-collector, respectively.



**Fig. 1.** Schematic diagram of the SI system for automated determination of Pu in environmental solids W1: 8 mol L<sup>-1</sup> HNO<sub>3</sub>; W2: 6 mol L<sup>-1</sup> HNO<sub>3</sub>; W3: 4, 2 or 1 mol L<sup>-1</sup> HNO<sub>3</sub>; W4: 9 mol L<sup>-1</sup> HCl; E1: 0.1 mol L<sup>-1</sup> NH<sub>2</sub>OH·HCl–2 mol L<sup>-1</sup> HCl; E2: 0.1, 0.5 or 1 mol L<sup>-1</sup> HCl; S1–S9: ports for sample loading; EF1–EF9: ports for eluate collection; Air: port for air aspiration to isolate the carrier from the solutions drawn into the holding coil; SP: syringe pump; SV-1–SV-5: selection valves; HC: holding coil; C1–C9: nine anion exchange columns.

### 2.2. Standards, reagents and samples

All reagents, including nitric acid (HNO<sub>3</sub>), hydrochloric acid (HCl), ammonium hydroxide (NH<sub>3</sub>·H<sub>2</sub>O), hydroxylammonium chloride (NH<sub>2</sub>OH·HCl), potassium disulfite (K<sub>2</sub>S<sub>2</sub>O<sub>5</sub>), sodium hydroxide (NaOH) and iron(III) chloride (FeCl<sub>3</sub>·6H<sub>2</sub>O) used in this work were of analytical reagent grade. Solutions attached to SV-1 in Fig. 1 are as follows: W1: 8 mol L<sup>-1</sup> HNO<sub>3</sub>, W2: 6 mol L<sup>-1</sup> HNO<sub>3</sub>, W3: 4, 2 or 1 mol L<sup>-1</sup> HNO<sub>3</sub> (depending upon the experimental conditions), W4: 9 mol L<sup>-1</sup> HCl, E1: 0.1 mol L<sup>-1</sup> NH<sub>2</sub>OH·HCl–2 mol L<sup>-1</sup> HCl, and E2: 0.1, 0.5 or 1 mol L<sup>-1</sup> HCl (depending upon the experimental conditions). All solutions were prepared using Milli-Q water (18 MΩ cm<sup>-1</sup>, Sartorius Stedim Biotech, Aubagne Cedex, France).

A stock solution of <sup>242</sup>Pu (0.1037 Bq g<sup>-1</sup> in 2 mol L<sup>-1</sup> HNO<sub>3</sub>) used as a chemical yield tracer of Pu was prepared by dilution of NBL-CRM 130 purchased from New Brunswick Laboratory (Argonne, IL). A <sup>239</sup>Pu standard solution of 0.100 Bq g<sup>-1</sup> in 2 mol L<sup>-1</sup> HNO<sub>3</sub> was supplied by Risø National Laboratory for Sustainable Energy (Denmark). Standard solutions of uranium and thorium were purchased from NIST (Gaithersburg, MD).

Anion exchange resins explored were of AG 1-type series with different crosslinkage and particle size, including AG 1-×2 (2% crosslinked, 50–100 mesh), AG 1-×4 (4% crosslinked, 50–100 mesh and 100–200 mesh) and AG 1-×8 (8% crosslinked, 50–100 mesh) in chloride form (Bio-Rad Laboratories Inc., Hercules, CA). AG 1 resins are strongly basic anion exchangers with quaternary ammonium functional groups attached to the styrenedivinylbenzene copolymer lattice. The resin was swelled in water and transferred into an Econo-Column® (Bio-Rad Laboratories Inc.) and pre-conditioned with HNO<sub>3</sub> of identical concentration as the sample loading medium. A handful of column sizes with varied aspect ratios and inner volume were investigated and compared in this work, including 10 mm i.d. × 20 cm long (ca. 16 mL), 7 mm i.d. × 20 cm long (ca. 8 mL), 7 mm i.d. × 10 cm long (ca. 4 mL), 5 mm i.d. × 10 cm long (ca. 2 mL), 7 mm i.d. × 5 cm long (ca. 2 mL) and 5 mm i.d. × 5 cm long (ca. 1 mL).

Three certified reference materials including soil (IAEA-375), sediment (IAEA-135) and seaweed (NIST-4359) [27] and two ref-

**Table 1**  
Comparison of different experimental conditions for the separation of Pu and the removal of interferences exploiting SI-anion exchange chromatography<sup>§</sup>.

Column size	Group	Resin <sup>a</sup>	Separation condition <sup>d</sup>	Chemical yield of <sup>242</sup> Pu, Y <sub>pu</sub> (%)	<sup>239</sup> Pu measured (Bq kg <sup>-1</sup> ) <sup>b,5</sup>	<sup>240</sup> Pu measured (Bq kg <sup>-1</sup> ) <sup>b,5</sup>	Decontamination factor <sup>c</sup>		
							<sup>238</sup> U	<sup>232</sup> Th	<sup>208</sup> Pb
16 mL (1.0 × 20 cm)	1–1	AG 1-×2	Washing sequence no. 1, 2.5 mL min <sup>-1</sup> Pu eluting solution no. 1, 1.0 mL min <sup>-1</sup>	102.3 ± 5.1	0.14 ± 0.01	0.10 ± 0.01	3.3 × 10 <sup>3</sup>	1.9 × 10 <sup>4</sup>	1.4 × 10 <sup>4</sup>
	1–2	AG 1-×4 (a)	Same as 1–1	99.9 ± 5.0	0.23 ± 0.02	0.08 ± 0.01	3.0 × 10 <sup>2</sup>	2.9 × 10 <sup>3</sup>	5.6 × 10 <sup>3</sup>
	1–3	AG 1-×8	Same as 1–1	96.4 ± 4.8	1.39 ± 0.14	0.11 ± 0.01	4.2 × 10 <sup>1</sup>	3.8 × 10 <sup>2</sup>	1.2 × 10 <sup>4</sup>
8 mL (0.7 × 20 cm)	2–1	AG 1-×2	Washing sequence no. 1, 2.5 mL min <sup>-1</sup> Pu eluting solution no. 2, 1.0 mL min <sup>-1</sup>	71.5 ± 3.6	0.12 ± 0.01	0.08 ± 0.01	1.1 × 10 <sup>3</sup>	5.2 × 10 <sup>3</sup>	3.1 × 10 <sup>4</sup>
	2–2	AG 1-×4 (a)	Same as 2–1	108.2 ± 5.4	0.16 ± 0.02	0.10 ± 0.01	1.6 × 10 <sup>3</sup>	6.4 × 10 <sup>3</sup>	3.9 × 10 <sup>3</sup>
	2–3	AG 1-×8	Same as 2–1	94.2 ± 4.7	0.16 ± 0.02	0.10 ± 0.01	3.2 × 10 <sup>2</sup>	7.8 × 10 <sup>2</sup>	8.1 × 10 <sup>3</sup>
4 mL (0.7 × 10 cm)	3–1	AG 1-×2	Same as 2–1	71.2 ± 3.6	0.12 ± 0.01	0.06 ± 0.01	2.1 × 10 <sup>3</sup>	4.4 × 10 <sup>3</sup>	1.1 × 10 <sup>4</sup>
	3–2	AG 1-×4 (a)	Same as 2–1	100.0 ± 5.0	0.12 ± 0.01	0.10 ± 0.01	1.3 × 10 <sup>3</sup>	2.4 × 10 <sup>3</sup>	2.2 × 10 <sup>4</sup>
	3–3	AG 1-×8	Same as 2–1	98.7 ± 4.9	0.16 ± 0.02	0.10 ± 0.01	1.0 × 10 <sup>3</sup>	8.9 × 10 <sup>2</sup>	8.6 × 10 <sup>3</sup>
2 mL (0.5 × 10 cm)	4–1	AG 1-×2	Washing sequence no. 2, 2.5 mL min <sup>-1</sup> Pu eluting solution no. 3, 2.5 mL min <sup>-1</sup>	75.0 ± 3.8	0.26 ± 0.03	0.08 ± 0.01	3.2 × 10 <sup>2</sup>	2.0 × 10 <sup>2</sup>	2.6 × 10 <sup>3</sup>
	4–2	AG 1-×4 (a)	Same as 4–1	103.0 ± 5.2	0.14 ± 0.01	0.09 ± 0.01	3.9 × 10 <sup>3</sup>	2.4 × 10 <sup>4</sup>	2.7 × 10 <sup>4</sup>
	4–3	AG 1-×8	Same as 4–1	98.1 ± 4.9	0.25 ± 0.03	0.09 ± 0.01	3.4 × 10 <sup>2</sup>	9.4 × 10 <sup>2</sup>	1.6 × 10 <sup>4</sup>
	4–4	AG 1-×2	Washing sequence no. 2, 5.0 mL min <sup>-1</sup> Pu eluting solution no. 3, 2.5 mL min <sup>-1</sup>	48.6 ± 2.4	0.15 ± 0.02	0.10 ± 0.01	8.9 × 10 <sup>2</sup>	6.8 × 10 <sup>2</sup>	9.3 × 10 <sup>3</sup>
	4–5	AG 1-×4 (a)	Same as 4–4	94.0 ± 4.7	0.25 ± 0.03	0.09 ± 0.01	3.9 × 10 <sup>2</sup>	6.7 × 10 <sup>3</sup>	1.6 × 10 <sup>4</sup>
	4–6	AG 1-×8	Same as 4–4	100.5 ± 5.0	0.23 ± 0.02	0.08 ± 0.01	4.8 × 10 <sup>1</sup>	2.1 × 10 <sup>2</sup>	2.9 × 10 <sup>4</sup>
	4–7	AG 1-×4 (a)	Washing sequence no. 2, 2.5 mL min <sup>-1</sup> Pu eluting solution no. 4, 2.5 mL min <sup>-1</sup>	92.1 ± 3.6	0.18 ± 0.02	0.12 ± 0.01	1.6 × 10 <sup>3</sup>	1.7 × 10 <sup>4</sup>	6.1 × 10 <sup>3</sup>
	4–8	AG 1-×4 (a)	Washing sequence no. 3, 2.5 mL min <sup>-1</sup> Pu eluting solution no. 4, 2.5 mL min <sup>-1</sup>	81.8 ± 4.1	0.17 ± 0.03	0.10 ± 0.01	2.1 × 10 <sup>3</sup>	1.3 × 10 <sup>4</sup>	7.5 × 10 <sup>3</sup>
	4–9	AG 1-×4 (a)	Washing sequence no. 4, 2.5 mL min <sup>-1</sup> Pu eluting solution no. 4, 2.5 mL min <sup>-1</sup>	80.2 ± 4.0	0.14 ± 0.01	0.09 ± 0.01	2.4 × 10 <sup>3</sup>	1.4 × 10 <sup>4</sup>	1.5 × 10 <sup>4</sup>
	4–10	AG 1-×4 (a)	Washing sequence no. 5, 2.5 mL min <sup>-1</sup> Pu eluting solution no. 4, 2.5 mL min <sup>-1</sup>	39.6 ± 2.0	0.14 ± 0.01	0.15 ± 0.02	2.6 × 10 <sup>3</sup>	1.1 × 10 <sup>4</sup>	9.4 × 10 <sup>3</sup>
	4–11	AG 1-×4 (a)	Washing sequence no. 6, 2.5 mL min <sup>-1</sup> Pu eluting solution no. 4, 2.5 mL min <sup>-1</sup>	31.0 ± 1.6	0.14 ± 0.01	0.15 ± 0.02	3.1 × 10 <sup>3</sup>	5.0 × 10 <sup>4</sup>	1.2 × 10 <sup>5</sup>
	4–12	AG 1-×4 (b)	Same as 4–1	88.4 ± 3.1	0.12 ± 0.02	0.08 ± 0.01	3.1 × 10 <sup>3</sup>	2.8 × 10 <sup>4</sup>	1.2 × 10 <sup>4</sup>
	4–13	AG 1-×4 (b)	Same as 4–7	91.6 ± 4.6	0.14 ± 0.01	0.10 ± 0.01	6.9 × 10 <sup>3</sup>	1.7 × 10 <sup>4</sup>	1.0 × 10 <sup>3</sup>
	4–14	AG 1-×4 (b)	Washing sequence no. 2, 2.5 mL min <sup>-1</sup> Pu eluting solution no. 5, 2.5 mL min <sup>-1</sup>	66.8 ± 3.3	0.14 ± 0.01	0.09 ± 0.01	8.6 × 10 <sup>3</sup>	1.2 × 10 <sup>4</sup>	1.0 × 10 <sup>3</sup>
	4–15	AG 1-×4 (b)	Washing sequence no. 2, 2.5 mL min <sup>-1</sup> Pu eluting solution no. 6, 2.5 mL min <sup>-1</sup>	78.5 ± 3.9	0.14 ± 0.01	0.07 ± 0.01	6.3 × 10 <sup>3</sup>	1.9 × 10 <sup>4</sup>	1.5 × 10 <sup>3</sup>

<sup>§</sup> Specific activities of <sup>239</sup>Pu, <sup>240</sup>Pu and <sup>242</sup>Pu are 2.3 × 10<sup>12</sup> Bq kg<sup>-1</sup>, 8.4 × 10<sup>12</sup> Bq kg<sup>-1</sup> and 1.46 × 10<sup>11</sup> Bq kg<sup>-1</sup>, respectively. The reference values of <sup>239</sup>Pu and <sup>240</sup>Pu concentrations in the Danish soil were reported to be 0.140 ± 0.008 and 0.098 ± 0.006 Bq kg<sup>-1</sup>, respectively.

<sup>a</sup> The particle sizes were 50–100 mesh for AG 1-×2, AG 1-×4 (a) and AG 1-×8 resins and 100–200 mesh for AG 1-×4 (b) resin.

<sup>b</sup> Experimental results are given as the average of three replicates ± standard deviation.

<sup>c</sup> The relative standard deviations were in all instances better than 10%.

<sup>d</sup> Washing sequence: no. 1: 200 mL of 8 mol L<sup>-1</sup> HNO<sub>3</sub> + 100 mL of 9 mol L<sup>-1</sup> HCl; no. 2: 100 mL of 8 mol L<sup>-1</sup> HNO<sub>3</sub> + 100 mL of 9 mol L<sup>-1</sup> HCl; no. 3: 100 mL of 6 mol L<sup>-1</sup> HNO<sub>3</sub> + 100 mL of 9 mol L<sup>-1</sup> HCl; no. 4: 100 mL of 4 mol L<sup>-1</sup> HNO<sub>3</sub> + 100 mL of 9 mol L<sup>-1</sup> HCl; no. 5: 100 mL of 2 mol L<sup>-1</sup> HNO<sub>3</sub> + 100 mL of 9 mol L<sup>-1</sup> HCl; no. 6: 100 mL of 1 mol L<sup>-1</sup> HNO<sub>3</sub> + 100 mL of 9 mol L<sup>-1</sup> HCl; Pu eluting solution: no. 1: 200 mL of 0.1 mol L<sup>-1</sup> NH<sub>2</sub>OH·HCl-2 mol L<sup>-1</sup> HCl; no. 2: 100 mL of 0.1 mol L<sup>-1</sup> NH<sub>2</sub>OH·HCl-2 mol L<sup>-1</sup> HCl; no. 3: 40 mL of 0.1 mol L<sup>-1</sup> NH<sub>2</sub>OH·HCl-2 mol L<sup>-1</sup> HCl; no. 4: 40 mL of 0.5 mol L<sup>-1</sup> HCl; no. 5: 40 mL of 0.1 mol L<sup>-1</sup> HCl; no. 6: 40 mL of 1.0 mol L<sup>-1</sup> HCl.

erence materials from round-robin laboratory inter-comparison tests, namely, a Danish soil [28] and an Irish Sea sediment, were analyzed through this work for evaluation of method trueness. Otherwise stated, the Danish soil was used in method development.

### 2.3. Sample pre-treatment

A certain amount of a given sample (depending on the concentration of Pu) was placed in a beaker and ashed at 550 °C overnight to decompose the organic matter. The ashed sample was spiked with 10 mBq (equal to 685 ng)  $^{242}\text{Pu}$  as a chemical yield tracer in the separation procedure. *Aqua regia* was added to the sample whereupon the mixture was digested on a hotplate at 150 °C for 30 min and 200 °C for 2 h, respectively. The beaker was covered with a watch-glass in the course of the digestion to prevent significant evaporation of the solution. After cooling, the supernatant was filtered through a GF/A filter to a centrifuge tube, the beaker and the filter-paper were washed with 30 mL of 0.2 mol L<sup>-1</sup> HCl. Ammonia was added to the supernatant to adjust the pH = 8–9 to co-precipitate Pu with iron hydroxides (for seaweed sample, a given amount (ca. 60 mg) of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was added to the sample before co-precipitation) and to remove matrix components including Ca and Mg. The co-precipitate was separated by centrifugation. A metered volume (ca. 30 mL) of 6 mol L<sup>-1</sup> NaOH was added to the precipitate to remove amphoteric elements, e.g., Al. For processing of large size samples, such as  $\geq 20$  g of seaweed or soil, the above co-precipitation steps with ammonia and NaOH were once again repeated before valence adjustment as described below.

### 2.4. Valence adjustment to Pu(IV)

Since tetravalent plutonium in nitric acid medium has the highest retention onto anion exchangers, a two-step valence adjustment was exploited hereby to ensure high absolute plutonium recoveries during the separation procedure [23,29]. Hydrochloric acid was added to the prior processed sample to dissolve the precipitate. 300 mg of  $\text{K}_2\text{S}_2\text{O}_5$  was then added and the solution was gently stirred for 10 min to reduce the overall Pu to Pu(III), whereupon NaOH was added to adjust pH to 10. The precipitate thus obtained was dissolved with concentrated  $\text{HNO}_3$ , with the consequent oxidation of Pu(III) to Pu(IV) by  $\text{NO}_2^-$  in the  $\text{HNO}_3$  solution. The solution was finally diluted to 8 mol L<sup>-1</sup>  $\text{HNO}_3$  prior to loading onto the anion exchange column.

### 2.5. Automated separation scheme

The SI-anion exchange chromatographic procedure consists of five steps as follows: I. Rinsing of the holding coil and sample inlet and outlet tubing with de-ionized water at a flow rate of 10 mL min<sup>-1</sup>; II. Pre-conditioning of the anion exchange resin with  $\text{HNO}_3$  of identical concentration as the sample loading at 3.0 mL min<sup>-1</sup>; III. Loading the sample (15 mL for the majority of samples, excepting 30 mL for 20 g of Danish soil, 50 mL for 20 g of seaweed and 75 mL for 50 g of Danish soil) in a 8 mol L<sup>-1</sup>  $\text{HNO}_3$  medium onto the anion exchange column at 1.0 mL min<sup>-1</sup> to retain the target analytes as anionic nitrate complexes [1]; IV. Rinsing of the column with 100–200 mL of 1–8 mol L<sup>-1</sup>  $\text{HNO}_3$  (depending on the experimental conditions, see Table 1) to remove most of the uranium and matrix elements, followed by 100 mL of 9 mol L<sup>-1</sup> HCl to remove thorium; V. Elution of Pu with 40–100 mL of 0.1–1.0 mol L<sup>-1</sup> HCl or 0.1 mol L<sup>-1</sup>  $\text{NH}_2\text{OH} \cdot \text{HCl}$  in 2 mol L<sup>-1</sup> HCl (depending on the experimental conditions, see Table 1). The flow rates for column rinsing and elution of Pu also varied within method development from 1.0 to 5.0 mL min<sup>-1</sup> and detailed information is presented in Table 1. Aiming at improving the speed of analysis in the method development, 9 samples (the maximum number

of samples that can be handled with the present system at a given run) were sequentially processed in a fully automated mode within the SI system by assembling 9 columns packed with anion exchange resins and altering the experimental conditions (e.g., washing and elution flow rates and the chemical composition of washing solutions and eluents) through the flexible control of the FIALab-associated software.

Each eluate was evaporated to dryness on a hot-plate. 5 mL of concentrated nitric acid was then added and the solution was heated to decompose  $\text{NH}_2\text{OH} \cdot \text{HCl}$  in the case of using 0.1 mol L<sup>-1</sup>  $\text{NH}_2\text{OH} \cdot \text{HCl}$ –2 mol L<sup>-1</sup> HCl as eluent and to eliminate HCl as well. The residue was reconstituted in 5 mL of 0.5 mol L<sup>-1</sup>  $\text{HNO}_3$  and analyzed by ICP-MS for quantification of  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{242}\text{Pu}$  and potential interfering nuclides.

### 2.6. Detection of Pu and other nuclides using ICP-MS

To 5 mL of processed sample (diluted in 0.5 mol L<sup>-1</sup>  $\text{HNO}_3$ ), 50  $\mu\text{L}$  of 100  $\mu\text{g L}^{-1}$  In(III) (as  $\text{InCl}_3$ ) was added as internal standard. The concentrations of  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{242}\text{Pu}$  as well as  $^{238}\text{U}$ ,  $^{232}\text{Th}$  and  $^{208}\text{Pb}$  were determined by inductively coupled plasma mass spectrometry (X Series<sup>II</sup>, Thermo Fisher Scientific, Waltham, MA) equipped with an Xs-skimmer cone and a concentric nebuliser under hot plasma conditions. The detection limits calculated as  $3\sigma$  of processing blank were 1.0 pg L<sup>-1</sup> for the overall Pu isotopes. A 0.5 mol L<sup>-1</sup>  $\text{HNO}_3$  solution was used as a washing solution between consecutive assays. No carry-over (memory effects) was observed for consecutive analysis of samples differing up to 3 orders of magnitude in Pu concentration. A least-squares regression line was used for quantification of Pu over the range of 0.01–100 ng L<sup>-1</sup>.

Prior to sample analyses, the ICP-MS instrument was tuned for maximum sensitivity of uranium using a 1  $\mu\text{g L}^{-1}$  solution of  $^{238}\text{U}$  in 0.5 mol L<sup>-1</sup>  $\text{HNO}_3$  and the instrumental parameters were further adjusted for Pu by analyzing a 1 ng L<sup>-1</sup>  $^{239}\text{Pu}$  solution. The typical operational conditions of the instrument are listed in our previous work in Table S-2 [23]. It is important to note that these parameters were optimized each time the instrument was initialized. Sensitivities ranged between  $1 \times 10^5$  and  $5 \times 10^5$  cps per  $\mu\text{g L}^{-1}$  of  $^{239}\text{Pu}$ .

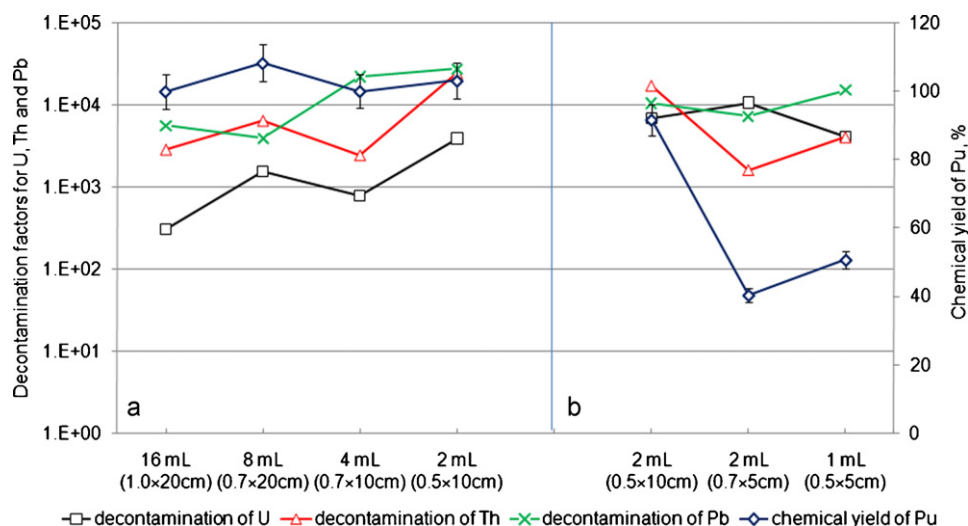
## 3. Results and discussion

### 3.1. Effect of column size and aspect ratio

Traditionally, large amount of anion exchange resin is often regarded essential for reliable separation of target radionuclides in environmental samples. Column volumes of 10–20 mL are commonly employed to ensure high absolute recoveries and appropriate separation efficiencies [12,18]. However, this give rise to relatively large resin consumption and consequently large amounts of acidic waste from column separation methods.

The separation efficiency of Pu with respect to chemical yield and decontamination of U, Th and Pb was investigated using different column dimensions. Decontamination factor for U, Th and Pb is defined as the ratio of the total amount of the interfering element in the sample solution loaded onto the column and the corresponding value in the eluate. Experimental results (see Fig. 2) reveal that columns of internal volume as large as ca. 16 mL ( $\phi 1.0 \times 20$  cm) are not necessary, and, in fact, small-sized anion exchange chromatographic columns ( $\phi 0.5 \times 10$  cm, ca. 2 mL) often suffice for the separation of Pu from 10 g of soil. The small-sized column provides the advantages of low consumption of resins and reagents for column washing and elution, therefore shortening the separation time and minimizing the generation of acidic waste. Shortening the packed column by half ( $\phi 0.5 \times 5$  cm, ca. 1 mL) resulted, how-





**Fig. 2.** Effect of column size on the chemical yield of Pu and decontamination factors for U, Th and Pb using (a) AG 1- $\times$ 4 (50–100 mesh) and (b) AG 1- $\times$ 4 (100–200 mesh) resins. (Sample: 10 g of Danish soil. The relative standard deviations for the decontamination factors for U, Th and Pb were in all instances better than 10%).

ever, inappropriateness because the chemical yield of Pu dropped dramatically to 50%. Therefore, a  $0.5 \times 10$  cm (ca. 2 mL) column was selected and integrated in the SI-manifold for isolation and determination of Pu isotopes in  $\geq 10$  g soil samples. To our best knowledge, this is the first report of the effect of column dimensions on the separation of Pu from large amounts of environmental samples using anion exchange chromatography.

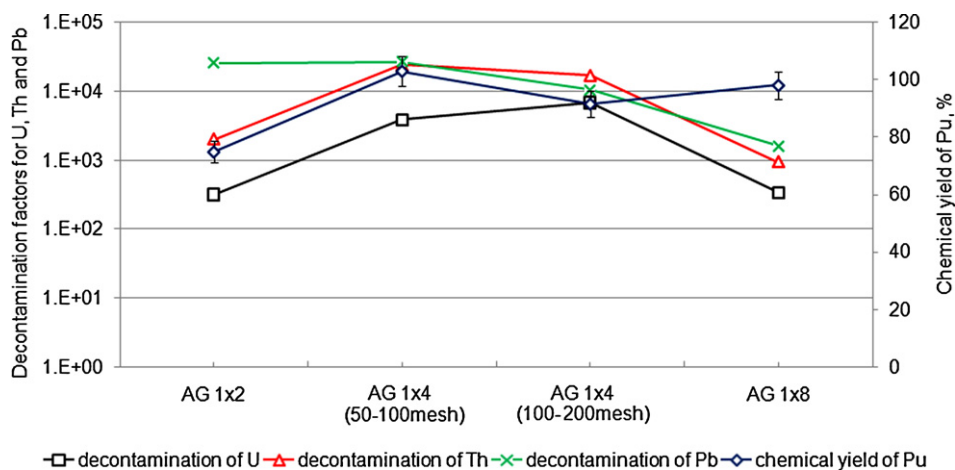
Besides column size, the column aspect ratio might also affect the performance of the SI-system. When using a ca. 2 mL-column packed with AG 1- $\times$ 4 (100–200 mesh) resin (see Fig. 2), the longer column with smaller diameter ( $\phi 0.5 \times 10$  cm) provided better recoveries of Pu compared with the shorter one with larger diameter ( $\phi 0.7 \times 5$  cm). This is in a good agreement with the plate theory model in chromatographic separations, that is, the longer the column for a given internal volume, the higher is the theoretical plate number and therefore the better the separation efficiency.

### 3.2. Effect of resin crosslinkage and particle size

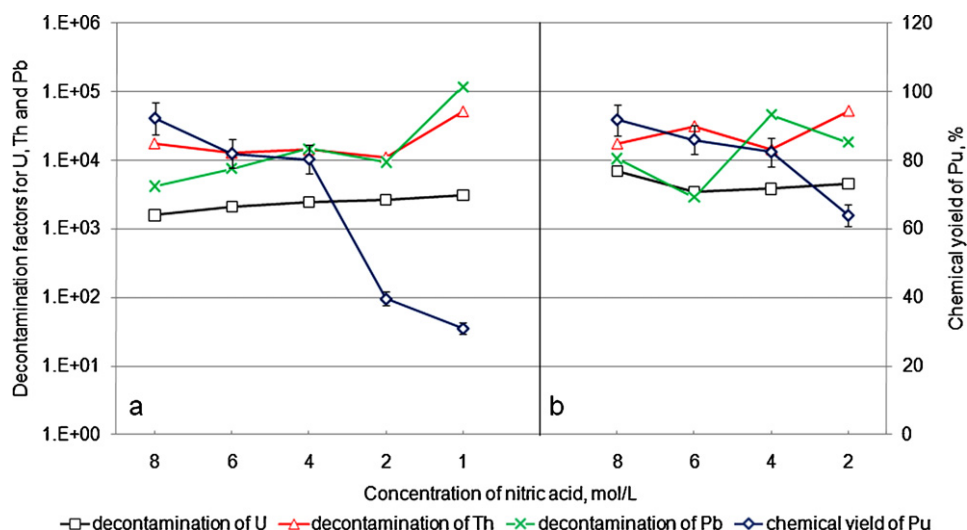
Crosslinkage is a measure of the percentage of divinylbenzene in the resin reaction mixture and affects the resin internal structure and therefore its swelling/shrinking properties. Three kinds of resins with different crosslinkage, namely AG 1- $\times$ 2, AG 1- $\times$ 4 and

AG 1- $\times$ 8, were tested and compared with regard to the chemical yields of Pu, concentrations of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  determined relative to the reference values and the decontamination factors for U, Th and Pb. The overall results are summarized in Table 1. When using the 16 mL column (see groups 1–1 to 1–3 in Table 1), chemical yields of Pu were in all instances better than 95%. The downscaling of the packed column however rendered chemical yields of Pu down to 70% for AG 1- $\times$ 2 resin, while still kept in the range of 90–100% for AG 1- $\times$ 4 and AG 1- $\times$ 8 resins. This indicates that the lower the anion exchanger crosslinkage the more significant is the influence of column size on the uptake of Pu under dynamic extraction conditions. This is most likely a consequence of the inferior anion exchange capacity of AG 1- $\times$ 2 resin ( $0.6 \text{ meq mL}^{-1}$ ) compared with AG 1- $\times$ 4 ( $1.0 \text{ meq mL}^{-1}$ ) and AG 1- $\times$ 8 ( $1.2 \text{ meq mL}^{-1}$ ) [30].

Of the three kinds of resins, the decontamination factors for U and Th were distinctly worsened by resorting to AG 1- $\times$ 8.  $^{239}\text{Pu}$  concentrations were thus significantly different from the reference values due to the low decontamination factors for U, which give rise to the interference from  $^{238}\text{U}^1\text{H}$  and the tailing of  $^{238}\text{U}$  at mass 239 in the ICP-MS measurement. The low decontamination factor for U might be raised from the undue amount of anion exchange moieties in AG 1-type highly cross-linked resins whereby increasing volumes of washing solutions would be needed under flow regime



**Fig. 3.** Effects of crosslinkage and particle size of AG1 type resins on chemical yields of Pu and decontamination factors for U, Th and Pb (Sample: 10 g of Danish soil; Column size: ca. 2 mL ( $\phi 0.5 \times 10$  cm); The relative standard deviations for the decontamination factors for U, Th and Pb were in all instances better than 10%).



**Fig. 4.** Effect of nitric acid concentration in the washing solution on the chemical yield of Pu and decontamination factors for U, Th and Pb for (a) AG 1 × 4 (50–100 mesh) and (b) AG 1 × 4 (100–200 mesh) resins (Sample: 10 g of Danish soil; Column size: ca. 2 mL  $\phi$ 0.5 × 10 cm; The relative standard deviations for the decontamination factors for U, Th and Pb were in all instances better than 10%).

for quantitative removal of sorbed interfering elements. AG 1-×2 performed better for the decontamination of U, Th and Pb compared with AG 1-×4 for the largest bead capacity column (ca. 16 mL). Decontamination factors were, however, improved for AG 1-×4 when downscaling the packed column. In fact, maximum decontamination factors for U, Th and Pb were obtained with AG 1-×4 in a ca. 2 mL column (see Fig. 3 and groups 4-1 to 4-3 in Table 1). A compromise in the number of functional moieties should thus be reached for efficient uptake of target species with minimal sorption of interfering nuclides.

Comparison of the sorptive behavior of the two types of particle sizes (50–100 mesh and 100–200 mesh) for AG 1-×4 resin revealed that with the exception of better decontamination factors for U (see groups 4-13 to 4-15 in Table 1), no improved performance using the resin with smaller particle size was observed with respect to the chemical yields of Pu, decontamination factors of Th and Pb and the accuracy in  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  determinations. In principle, the smaller the particle size of the resin, the more favorable is the ion exchange kinetics [31]. However, quantitative uptake of Pu might be accomplished in either case at the sample loading flow rates in the SI system. Therefore, no remarkable difference should be expected regarding chemical yields of Pu. The improved decontamination factors for U are the result of the larger specific surface area in 100–200 mesh resin, which thus gives rise to a better chromatographic separation between U and Pu. Yet, an undue increase of flow backpressure was occasionally observed in the SI-column system when using small bead particles, which suggests that a precise control of sample/elution flow rate

### 3.3. Removal of interferences

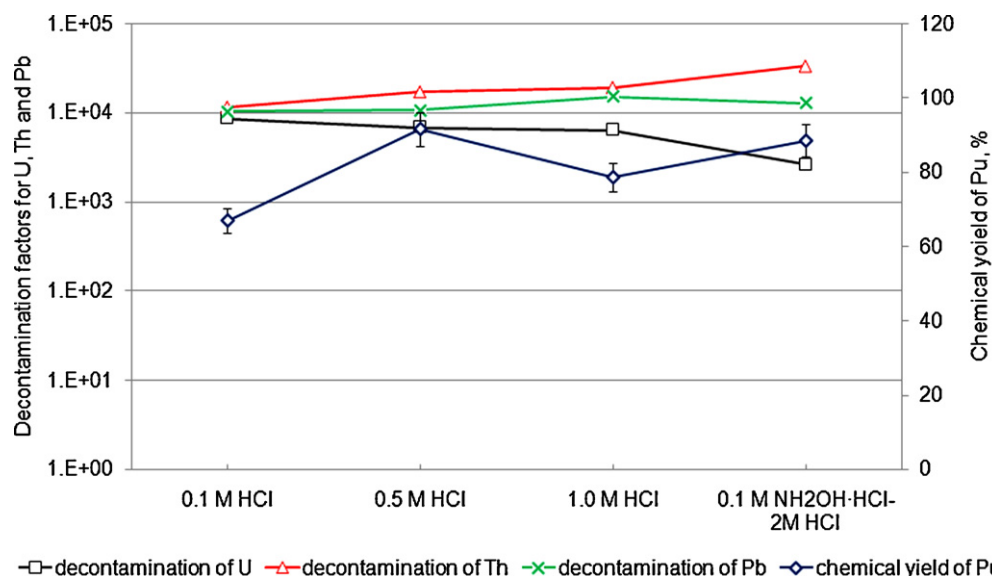
As mentioned above, large amounts of concomitant  $^{238}\text{U}$  and isotopes of Pb might prevent accurate quantification of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  by ICP-MS because of isobaric interferences of the polyatomic ions  $^{238}\text{U}^1\text{H}$ ,  $^{238}\text{U}^2\text{H}$ ,  $^{208}\text{Pb}^{31}\text{P}$ ,  $^{204}\text{Pb}^{35}\text{Cl}$ ,  $^{206}\text{Pb}^{33}\text{S}$  and tailing of  $^{238}\text{U}$  in the 239 mass region. In addition,  $^{229}\text{Th}$ ,  $^{230}\text{Th}$  and  $^{234}\text{U}$  would interfere with the eventual detection of  $^{242}\text{Pu}$  by alpha spectrometry and similarly  $^{228}\text{Th}$  interfere with  $^{238}\text{Pu}$ . In order to improve the decontamination factors of these potentially interfering elements, different washing sequences and flow rates were investigated for AG 1-×4 resin (50–100 mesh and 100–200 mesh). Experimental results (see Fig. 4) demonstrated that the lower the concentration of nitric acid in the washing solution, the slightly better were the decontamination factors for the investigated interfering species. However, the chemical yields of Pu dropped dramatically with the decrease in nitric acid concentration, especially with the use of AG 1-×4 (50–100 mesh). 8 mol L<sup>-1</sup> HNO<sub>3</sub> was selected as the optimum solution for the first washing step in terms of chemical yields and decontamination factors for U, which is in good agreement with previously published works [12]. According to our earlier findings [23], 9 mol L<sup>-1</sup> HCl was selected for the removal of Th from anion exchangers, and decontamination factors of  $>10^4$  for Th were encountered.

Of the decontamination of interfering elements, the removal of  $^{238}\text{U}$  is the most critical issue for the accurate quantification of Pu isotopes, especially  $^{239}\text{Pu}$ . Hereby, the interference factor

$$\left( \text{IF} = \frac{\text{corresponding } ^{239}\text{Pu concentration (ppt)}}{\text{uranium concentration (ppt)}} = \frac{\text{measured signal in mass 239 (cps)}}{\text{signal of mass 238 in U solution (cps)}} \right)$$

$\leq 1.0 \text{ mL min}^{-1}$  is here mandatory. To sum up, the resin with smaller particle size, viz. AG 1-×4 (100–200 mesh), is recommended especially in the case of analysis of environmental samples with high U levels to ensure sufficient removal of  $^{238}\text{U}$  and accurate detection of  $^{239}\text{Pu}$ . On the contrary, the use of AG 1-×4 (50–100 mesh) in SI anion chromatography is recommended when dealing with samples with low U concentration using high flow rates for column rinsing and elution. Because of minimal flow impedance it should be the sorbent of choice in long-term unattended monitoring schemes.

was defined as the combined contribution ratio of  $^{238}\text{U}$ , including polyatomic ion  $^{238}\text{U}^1\text{H}$  and tailing, to 239 mass region in ICP-MS measurement. In this work, the interference factor of  $^{238}\text{U}$  was measured to be  $10^{-5}$ , that is, if the ratio between the concentration of  $^{239}\text{Pu}$  and  $^{238}\text{U}$  in the eluate is  $\geq 10^{-3}$ , the interference of  $^{238}\text{U}$  in the detection of  $^{239}\text{Pu}$  will be less than 1%. Therefore, the criteria for evaluating the decontamination of U could be calculated according to the interference factor and the level of U and Pu in the sample. Using 10 g of Danish soil for example, the level of U and  $^{239}\text{Pu}$  in the prepared sample solution (15 mL) is around  $0.3 \text{ mg L}^{-1}$  and  $0.04 \text{ ng L}^{-1}$ , respectively. If the decontamination factor would be



**Fig. 5.** Effect of eluent composition on chemical yield of Pu and decontamination factors for U, Th and Pb (Sample: 10 g of Danish soil; Resin: AG 1- $\times$ 4 (100–200 mesh); Column size: ca. 2 mL ( $\phi$ 0.5  $\times$  10 cm); The relative standard deviations for the decontamination factors for U, Th and Pb were in all instances better than 10%).

better than  $2 \times 10^3$  and the chemical yield of Pu higher than 80%, the concentrations of  $^{238}\text{U}$  and  $^{239}\text{Pu}$  in the eluate will be  $150 \text{ ng L}^{-1}$  and  $0.03 \text{ ng L}^{-1}$ , respectively. Hence, the interfering effect of  $^{238}\text{U}$  in  $^{239}\text{Pu}$  determination would be  $\leq 5\%$ . Therefore, it is possible to state that the decontamination of U under the optimum experimental conditions in this work basically meets the analytical requirements for analysis of real-life environmental solids.

In general, the decontamination factors for  $^{238}\text{U}$  using anion exchange resins in this work were generally lower by a factor of 10–100 compared with those of TEVA resin [23]. This can be explained by the fact that uranium has a relatively high distribution coefficient (in the order of 10–20) on anion exchange resins in highly concentrated nitric acid media e.g.,  $8 \text{ mol L}^{-1} \text{ HNO}_3$ , and is not readily washed away; while the binding of uranium to TEVA<sup>®</sup> resin is weaker (distribution coefficient in the order of 1–2) under the optimum conditions for uptake of Pu (namely,  $1 \text{ mol L}^{-1} \text{ HNO}_3$  [23]). In case of processing samples with high level concentrations of U by resorting of anion exchange chromatography, a supplementary column might still be required for obtaining highly purified eluates. For example, by means of combining an extraction chromatographic step exploiting UTEVA/TRU with anion exchange chromatography (AG 1- $\times$ 8), Lindahl et al. [19] achieved a U decontamination factor of  $1.2 \times 10^4$  for determining Pu isotopes in small-sized marine samples ( $\leq 2 \text{ g}$  of coral or  $\leq 20 \text{ L}$  seawater).

The higher the flow rates for column rinsing, the faster the separation procedure. Yet, decontamination factors for U, Th and Pb were deteriorated whenever column washing of AG 1- $\times$ 4 was executed at  $5.0 \text{ mL min}^{-1}$  instead of  $2.5 \text{ mL min}^{-1}$  (see groups 4.2 and 4.5 in Table 1). Therefore the flow rate for washing solutions was set to  $2.5 \text{ mL min}^{-1}$  for the remainder of the work.

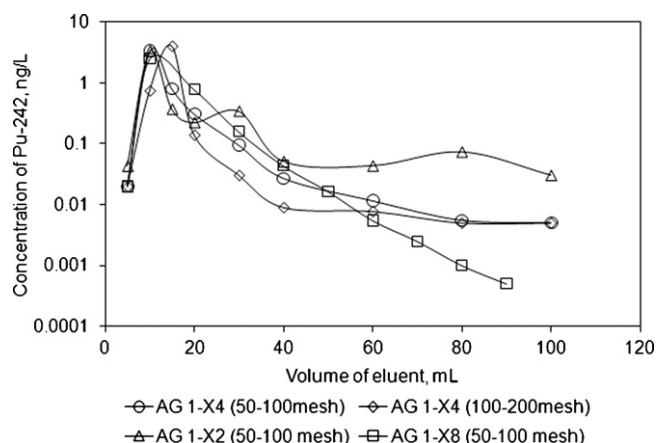
### 3.4. Elution of Pu

In previous publications [12,32],  $0.1 \text{ mol L}^{-1} \text{ NH}_2\text{OH-HCl}$  in  $2 \text{ mol L}^{-1} \text{ HCl}$  was utilized for efficient elution of Pu from anion exchange chromatographic columns, which is based on the on-column reduction of Pu(IV) to the non-adsorbable Pu(III), and retrieval of Pu(III) from the anion exchanger. However, the use of  $\text{NH}_2\text{OH-HCl}$  and large amounts of HCl could worsen the measurement efficiency of Pu by ICP-MS as well as introduce chloride-related interferences. Some authors have exploited alter-

native eluents based on the low sorptive capacity of Pu(IV) complexes formed with these eluents onto anion exchangers, but without reducing Pu(IV) to Pu(III), e.g., diluted HF along with  $\text{HNO}_3$  or HCl, diluted HCl, or diluted  $\text{H}_2\text{C}_2\text{O}_4\text{-HNO}_3$  solution. However, our preliminary investigations revealed that the decontamination of U would be deteriorated when the eluent was prepared in diluted  $\text{HNO}_3$ . Besides HF might damage the ICP-MS nebulizer and torch, and oxalates have the potential risk of forming black carbon grains in the torch due to incomplete decomposition. Therefore, potential in-line coupling of anion-exchange chromatography with ICPMS is not feasible using either eluent.

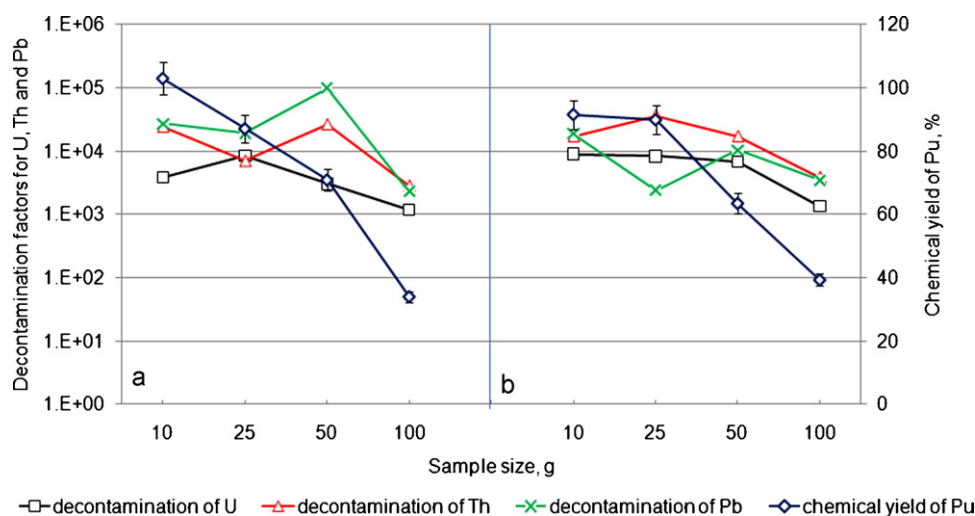
HCl solutions in the concentration range of  $0.1\text{--}1.0 \text{ mol L}^{-1}$  were assessed for the elution of Pu. Experimental results for AG 1- $\times$ 4 (100–200 mesh) resin (see Fig. 5) revealed better decontamination factors for U and slightly lower decontamination of Th using HCl as compared with those using  $0.1 \text{ mol L}^{-1} \text{ NH}_2\text{OH-HCl}$  in  $2 \text{ mol L}^{-1} \text{ HCl}$ . Of the four conditions for Pu elution illustrated in Fig. 5, improved chemical yields of Pu were obtained using either  $0.5 \text{ mol L}^{-1} \text{ HCl}$  or  $0.1 \text{ mol L}^{-1} \text{ NH}_2\text{OH-HCl}$  in  $2 \text{ mol L}^{-1} \text{ HCl}$ . Yet, decontamination factors for U, Th and Pb in AG 1- $\times$ 4 (50–100 mesh) were worsened using  $0.5 \text{ mol L}^{-1} \text{ HCl}$  as compared with  $0.1 \text{ mol L}^{-1} \text{ NH}_2\text{OH-HCl}$  in  $2 \text{ mol L}^{-1} \text{ HCl}$  (see group 4-2 and 4-7 in Table 1). This is attributed to the low distribution constants of uranium and lead onto AG 1- $\times$ 4 (50–100 mesh) in diluted hydrochloric acid solutions, whereby the remainders of U and Pb on the resin were co-eluted with Pu in the eluate. Finally,  $0.5 \text{ mol L}^{-1} \text{ HCl}$  was selected as eluent for Pu in this work due to advantages of absence of salts and potential direct injection into ICP-MS. However, care should also be paid to the in-line injection of eluate into ICP-MS when processing samples containing high level concentrations of lead and/or mercury, since the formation of polyatomic ions, such as  $^{204}\text{Pb}^{35}\text{Cl}$  and  $^{202}\text{Hg}^{37}\text{Cl}$ , might cause interferences in the detection of  $^{239}\text{Pu}$ .

Traditionally, a large amount of solvent, such as 100–200 mL, is used for quantitative elution of Pu, which makes the elution procedure very tedious and time consuming. In order to select an appropriate volume of eluent without deterioration of chemical yields of Pu, the elution profiles of Pu were investigated. A severe tailing effect was observed in all cases for different crosslinked resins (see Fig. 6), therefore, at least 40 mL of  $0.5 \text{ mol L}^{-1} \text{ HCl}$  was deemed necessary for efficient elution of Pu from AG 1- $\times$ 4. Our preliminary investigations also confirmed that no improvement in speeding up the elution procedure was obtained with  $0.1 \text{ mol L}^{-1}$



**Fig. 6.** Elution curves of Pu for AG 1-type resins (Sample: 10 g of Danish soil; Column size: ca. 2 mL ( $\phi 0.5 \times 10$  cm); eluent:  $0.5 \text{ mol L}^{-1}$  HCl, flow rate:  $2.5 \text{ mL min}^{-1}$ ).

$\text{NH}_2\text{OH}\cdot\text{HCl}$ – $2 \text{ mol L}^{-1}$  HCl as eluent, because  $\geq 40 \text{ mL}$  were also needed for quantitative elution of Pu from a 2 mL column for all the anion exchangers. The large volume of eluate needs to be reduced prior to ICP-MS detection, and hence off-line measurements were conducted in this work. The eluate was firstly evaporated to dryness and reconstituted in  $0.5 \text{ mol L}^{-1}$   $\text{HNO}_3$  as detailed under Section 2.



**Fig. 7.** Investigation of the performance of (a) AG 1-x4 (50–100 mesh) and (b) AG 1-x4 (100–200 mesh) resins for uptake of Pu and interfering nuclides at varied sample amounts (Sample: 10–100 g of Danish soil; Column size: ca. 2 mL ( $\phi 0.5 \times 10$  cm); The relative standard deviations for the decontamination factors for U, Th and Pb were in all instances better than 10%).

**Table 2**

Analytical results of certified/standard reference materials and reference samples<sup>a</sup>.

Sample name	Chemical yield, %	$^{239}\text{Pu}$ measured, Bq $\text{kg}^{-1}$	$^{240}\text{Pu}$ measured, Bq $\text{kg}^{-1}$	$^{239}\text{Pu}+^{240}\text{Pu}$ measured, Bq $\text{kg}^{-1}$	Certified or reported concentration, Bq $\text{kg}^{-1}$		
					$^{239}\text{Pu}$	$^{240}\text{Pu}$	$^{239}+^{240}\text{Pu}$
IAEA-375 soil	$89.3 \pm 3.5$	$0.12 \pm 0.02$	$0.13 \pm 0.02$	$0.30 \pm 0.04$	$0.113 \pm 0.010$ [32]	$0.124 \pm 0.020$ [32]	$0.30(0.26\text{--}0.34)^*$
IAEA-135 sediment	$69.3 \pm 2.5$	$125.9 \pm 8.6$	$95.4 \pm 8.3$	$221.4 \pm 16.9$	$123.0 \pm 3.8$ [31]	$93.8 \pm 2.3$ [31]	$213(205\text{--}226)^*$
NIST-SRM-4359 seaweed	$72.5 \pm 3.1$	$0.079 \pm 0.003$	$0.052 \pm 0.005$	$0.131 \pm 0.008$	$0.084 \pm 0.003$ *	$0.057(0.049\text{--}0.066)$ [27]	$0.130 \pm 0.008^*$
Irish Sea sediment	$59.2 \pm 5.1$	$228.9 \pm 0.4$	$172.3 \pm 0.9$	$401.7 \pm 1.2$	$237.0 \pm 5.0$ [31]	$181.0 \pm 4.9$ [31]	$419.0 \pm 10.6$ [31]
Danish soil	$90.5 \pm 3.0$	$0.15 \pm 0.02$	$0.09 \pm 0.01$	$0.24 \pm 0.03$	$0.140 \pm 0.008$ [28]	$0.098 \pm 0.006$ [28]	$0.238 \pm 0.014$ [28]

<sup>a</sup>Values are the average of twenty replicates ( $\pm$ standard deviation) for Danish soil and the average of three replicates ( $\pm$ standard deviation) for the other samples.

\*Certified values.

### 3.5. Recommended separation procedure

The optimized separation procedure using anion exchange chromatography in an automated SI fashion is summarized as follows:

- Rinsing of holding coil and sample inlet and outlet tubing with Milli-Q water at  $10 \text{ mL min}^{-1}$ .
- Pre-conditioning a ca. 2 mL (5 mm i.d.  $\times$  10 cm long) column of AG 1-x4 (50–100 or 100–200 mesh) anion exchange resin with  $8 \text{ mol L}^{-1}$   $\text{HNO}_3$  at  $3.0 \text{ mL min}^{-1}$ .
- Loading the sample solution in  $8 \text{ mol L}^{-1}$   $\text{HNO}_3$  onto the anion exchange column at  $1.0 \text{ mL min}^{-1}$ .
- Rinsing of the column with 100 mL of  $8 \text{ mol L}^{-1}$   $\text{HNO}_3$  to remove most of the uranium and matrix elements, followed by 100 mL of  $9 \text{ mol L}^{-1}$  HCl to remove thorium at  $2.5 \text{ mL min}^{-1}$ .
- Elution of Pu with 40 mL of  $0.5 \text{ mol L}^{-1}$  HCl at  $2.5 \text{ mL min}^{-1}$ .

### 3.6. Separation capability of the anion exchange resin and sample throughput

The analytical results (see Fig. 7) demonstrated that up to 50 g soil can be processed with a ca. 2 mL of AG 1-x4 resin of both 50–100 mesh and 100–200 mesh. To our best knowledge, this is the first work where as much as 50 g of environmental solids are handled using a small-sized anion exchange column housed in an SI network, which reveals the relative high separation capacity of AG 1-x4 for Pu. When the sample size was increased to 100 g, the chemical yield of Pu however decreased dramatically down to 40%.



In general, we recommend to analyze samples  $\leq 25$  g regardless of the resin particle size (see Fig. 7), since both the chemical yield of Pu and decontamination factor for U slightly decreased when increasing the sample size, which might induce the potential risk of inaccurate quantification of Pu.

Compared with a previously published report in which  $\leq 10$  g of soil samples were processed [26], the enrichment factors in this work could be  $\geq 5$  fold better and thus also the minimum detectable concentrations of Pu isotopes. Moreover, merely one small-sized column sufficed the entire chemical separation. The automated SI manifold is more readily compatible to accommodate multi-stage analytical procedures compared with the two-column associated protocols reported earlier in the literature [12,18].

The total on-column separation procedure takes less than 2.5 h for a single sample. Thus, nine samples can be sequentially processed in a fully automated mode within one day, which otherwise would be very tedious and labor-intensive, and in parallel with the pre-treatment of the next batch of 9 samples in a batch-wise fashion. As a result, the sample throughput is significantly improved compared with the traditional manual method, wherein 2–3 days are needed for processing similar sample amounts because sample treatment and column separation are commonly performed sequentially. Besides, the SI-based multi-stage analytical procedure performed stably and robustly within a long-term continuous operation suggesting its actual applicability to the rapid analysis of large number of samples within a short time frame, as demanded in emergency situations.

### 3.7. Method validation and application

Three standard/certified reference materials including 5 g of IAEA-375 soil, 1 g of IAEA-135 sediment and 20 g of NIST-4359 seaweed, and two samples, namely, a Danish soil (10 g) and an Irish Sea sediment (0.5 g), were analyzed in this work. The concentrations of Pu isotopes measured in the above solid materials are presented in Table 2.  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  concentrations obtained for the overall samples are in good agreement with the certified values or data reported earlier in the literature.

The reproducibility was assessed through the analysis of twenty Danish soil samples (10 g each) and the results obtained revealed an average chemical yield of 90.5% with an RSD of 3.0% and an average  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  concentrations of 0.15 and 0.09 Bq kg $^{-1}$  with an SD of 0.02 and 0.01, respectively (see Table 2). The good agreement of the measured values for  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  concentrations with the reference values ( $^{239}\text{Pu}$ :  $0.140 \pm 0.008$  Bq kg $^{-1}$ ;  $^{240}\text{Pu}$ :  $0.098 \pm 0.006$  Bq kg $^{-1}$ ) demonstrates the satisfactory true-ness and reproducibility of the developed analytical method.

## 4. Conclusion and perspective

An automated analytical method using anion exchange chromatography in an SI-based flow setup was developed for rapid determination of Pu isotopes in largesized environmental samples. The effect of chemical and physical properties of the anion exchange resin on the separation efficiency was thoroughly investigated aiming at the optimization of the experimental conditions. A small-sized 2 mL-column packed with AG 1- $\times$ 4 resin was selected and optimum column rinsing and elution procedures were recommended for accurate determination of Pu in environmental solids. Investigation of column sorptive capacity reveals that up to 50 g of soil sample can be processed. The total column separation process for a single sample is  $\leq 2.5$  h, which, in turn, saves analytical time and reduces the labor intensity of manual anion exchange methods and enables its application to emergency situations.

A direction of our future work could be further improving the sample throughput of the proposed SI system via replacement of

the syringe pump with a multiple channel (multi-syringe) pump and increasing the number of rotary valves to enable the automatic processing of more than two samples at a time. Another direction worth exploring would be the simultaneous determination of Pu isotopes and  $^{237}\text{Np}$  using the developed method and  $^{242}\text{Pu}$  as a tracer, since  $^{237}\text{Np}$  behaves similarly as Pu isotopes under given experimental conditions onto anion exchange resins.

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## Paper III

Qiao, J. X., Hou, X. L., Roos, P., Miró, M. Rapid Determination of plutonium isotopes in environmental samples using sequential injection extraction chromatography and detection by inductively coupled plasma mass spectrometry. *Analytical Chemistry*. 2009, 81, 8185-8192.

# Rapid Determination of Plutonium Isotopes in Environmental Samples Using Sequential Injection Extraction Chromatography and Detection by Inductively Coupled Plasma Mass Spectrometry

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This article presents an automated method for the rapid determination of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  in various environmental samples. The analytical method involves the in-line separation of Pu isotopes using extraction chromatography (TEVA) implemented in a sequential injection (SI) network followed by detection of isolated analytes with inductively coupled plasma mass spectrometry (ICP-MS). The method has been devised for the determination of Pu isotopes at environmentally relevant concentrations, whereby it has been successfully applied to the analyses of large volumes/amounts of samples, for example, 100–200 g of soil and sediment, 20 g of seaweed, and 200 L of seawater following analyte preconcentration. The investigation of the separation capability of the assembled SI system revealed that up to 200 g of soil or sediment can be treated using a column containing about 0.70 g of TEVA resin. The analytical results of Pu isotopes in the reference materials showed good agreement with the certified or reference values at the 0.05 significance level. Chemical yields of Pu ranged from 80 to 105%, and the decontamination factors for uranium, thorium, mercury and lead were all above  $10^4$ . The duration of the in-line extraction chromatographic run was  $<1.5$  h, and the proposed setup was able to handle up to 20 samples (14 mL each) in a fully automated mode using a single chromatographic column. The SI manifold is thus suitable for rapid and automated determination of Pu isotopes in environmental risk assessment and emergency preparedness scenarios.

Pu isotopes including  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  are regarded as highly hazardous environmental pollutants due to their radiological toxicities and extremely long radioactive half-lives, which lead to long-term persistence in the environment. There are a number of sources of plutonium in the environment, including nuclear weapons testing in the 1950ies–1980ies, controlled releases from the operation of nuclear power plants and nuclear

reprocessing facilities and nuclear accidents. It has been reported that more than  $10^{16}$  Bq of  $^{239+240}\text{Pu}$  have been already released into the environment.<sup>1,2</sup> Accurate determination of Pu isotopes, often conducted in a large number of samples, is important in radioecological studies and environmental risk assessment. In most cases, the concentrations of Pu isotopes are at low or ultralow levels ( $<10^{-12}$  g/g or  $10^{-12}$  g/L). In emergency situations, such as nuclear accidents and in connection with potential nuclear terrorism, rapid analysis of samples is required. Pu isotopes are normally measured by alpha spectrometry and mass spectrometry (especially ICP-MS). However, as a consequence of the extremely low concentrations of Pu isotopes in environmental samples, adverse effects of matrix components and isobaric interferences in ICP-MS, and interfering alpha emitters in alpha spectrometry, the preconcentration of plutonium isotopes from matrix ingredients and the chemical separation from interfering radionuclides and stable isotopes have to be implemented before measurement. A number of traditional methods for the preconcentration and separation of Pu using coprecipitation, liquid–liquid extraction, ion exchange chromatography, and often sequential combinations of these methods have been reported over the past six decades and applied to the analysis of environmental and biological samples.<sup>3–5</sup> Although the above-mentioned methods are normally accurate and sensitive, most of them are operated manually and are therefore tedious, time-consuming, and labor-intensive. For example, the determination of plutonium in 4–8 samples normally takes up to 3–4 days excluding 5–20 days of measurement time using alpha spectrometry.<sup>4</sup> Moreover, traditional methods usually

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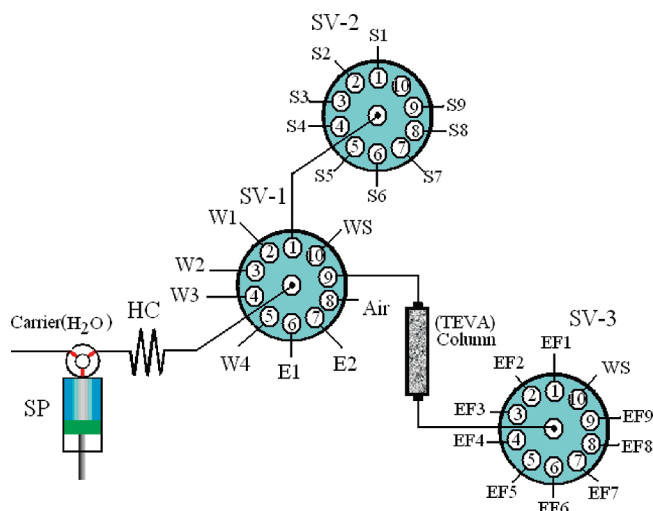
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require large volumes of organic solvents and mineral acids and embody the risk of low decontamination factors. This remains inevitably the bottleneck for rapid analysis of a large number of samples in risk assessment studies and emergency situations. Extraction chromatographic methods using distinct selective sorbent materials, such as TEVA,<sup>6–10</sup> TRU<sup>11–14</sup> and Diphonix<sup>15,16</sup> resins (Eichrom) are becoming an attractive option for the determination of Pu in environmental samples. Liquid chromatographic assays have been reported by several groups,<sup>17–20</sup> but the reliability of the separation procedure is often impaired by the limited column separation capability and matrix effects. A vacuum box system has also been developed for the rapid determination of Pu in environmental samples,<sup>21,22</sup> but manual operation and maintenance is still needed and therefore lacks automation.

Over the past few years, attention has been paid to the development of automatic methods involving extraction chromatography for determination of Pu based on flow injection (FI) and sequential injection (SI) approaches.<sup>3</sup> Most of these methods reported so far were however merely applied to the analysis of highly contaminated samples whereby samples of small size were handled, for example, soils, sediments of less than 1 g, and seawater or effluents (such as nuclear wastewater) of less than 5 L.<sup>23–31</sup> This might be a consequence of the downscaling of standard column separation procedures in an FI/SI fashion, which might be inappropriate for separation of Pu from large amounts of samples, often tens to hundreds of L/g, as required for sensitive



**Figure 1.** Schematic diagram of the SI system for determination of Pu isotopes. W1, 1 mol/L HNO<sub>3</sub>; W2, 2 mol/L HNO<sub>3</sub>; W3, 6 mol/L HCl; W4, 9 mol/L HCl; E1, 0.1 mol/L NH<sub>2</sub>OH·HCl–2 mol/L HCl; and E2, 0.1 mol/L NH<sub>2</sub>OH·HCl–0.1 mol/L HNO<sub>3</sub>. WS, waste; S1–S9, ports for sample loading; EF1–EF9, ports for eluate collection; air, port for air aspiration to isolate the carrier from the solutions drawn into the holding coil; SP, syringe pump; SV, selection valve; HC, holding coil.

quantification of Pu at environmentally relevant levels. In several FI/SI works, the decontamination factors for matrix elements and interfering radionuclides or the chemical yields of Pu are not stable enough for accurate analysis.<sup>3</sup> The progressive degradation of the sorbent material during repetitive use and sample cross-contamination are other well-known limitations of previously published FI/SI systems with permanent columns.<sup>3</sup> To our best knowledge, no versatile FI/SI analytical method has been reported to date for automated determination of Pu isotopes in distinct environmental samples, for example, large amounts of seaweed, soil, sediment, and water samples. Moreover, the putative continuous operation and the robustness of SI-extraction chromatographic systems have not yet been investigated.

To overcome the above-mentioned drawbacks of downscaled FI/SI assemblies, we herein develop and validate an SI-extraction chromatographic method for expeditious determination of Pu isotopes in large volumes/amounts of environmental samples (>10 g of soil, sediment, and seaweed and up to 100–200 L of seawater).

## EXPERIMENTAL SECTION

**Instrumentation.** The automated separation setup consisted of an FIALab-3500B SI system (FIALab Instruments, Bellevue, WA) furnished with a syringe pump (SP, Cavo, Sunnyvale, CA, 25 mL capacity), an internal 10-port multiposition selection valve (SV-1), two external 10-port multiposition section valves, SV-2 and SV-3 (Valco Instruments, Houston, TX), and a separation column. A schematic illustration of the SI analyzer is shown in Figure 1. The system was computer controlled via the FIALab software. All the outlets of the selection valve (SV-1) were connected through PEEK ferrules and fittings with rigid PTFE tubing (2.4 mm i.d./3.2 mm o.d.) and all the outlets of the external selection valves (SV-2 and SV-3) were connected through PEEK ferrules and fittings with rigid PTFE tubing of smaller diameter (0.8 mm i.d./1.6 mm o.d.). The central port of the SV-1 was connected to the holding coil (HC), which consisted of a 6.6 m long PTFE tubing with an inner

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capacity of 30 mL (2.4 mm i.d./3.2 mm o.d.). Hereby, it should be mentioned that the two external selection valves, that is, SV-2 and SV-3, can be also replaced by an autosampler and eluate autocollector, respectively.

**Standards, Reagents, and Samples.** All reagents, including nitric acid ( $\text{HNO}_3$ ), hydrochloric acid ( $\text{HCl}$ ), ammonium hydroxide ( $\text{NH}_4\text{OH}$ ), hydroxylammonium chloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ), sodium nitrite ( $\text{NaNO}_2$ ), potassium disulfite ( $\text{K}_2\text{S}_2\text{O}_5$ ), sodium hydroxide ( $\text{NaOH}$ ), ferric chloride ( $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ ), and ascorbic acid used in the experiment were of analytical reagent grade. Solutions presented in Figure 1 were W1, 1 mol/L  $\text{HNO}_3$ ; W2, 2 mol/L  $\text{HNO}_3$ ; W3, 6 mol/L  $\text{HCl}$ ; W4, 9 mol/L  $\text{HCl}$ ; E1, 0.1 mol/L  $\text{NH}_2\text{OH}\cdot\text{HCl}$ –2 mol/L  $\text{HCl}$ ; and E2, 0.1 mol/L  $\text{NH}_2\text{OH}\cdot\text{HCl}$ –0.1 mol/L  $\text{HNO}_3$ .

Solutions of  $^{242}\text{Pu}$  (0.1037 Bq/g in 2 mol/L  $\text{HNO}_3$ ) diluted from NBL-CRM 130 and used as a chemical yield tracer of plutonium, and  $^{243}\text{Am}$  (0.1024 Bq/g in 2 mol/L  $\text{HNO}_3$ ) prepared from NBL-CRM 127 were both purchased from New Brunswick Laboratory (Argonne, IL).  $^{239}\text{Pu}$  solution of 0.100 Bq/g in 2 mol/L  $\text{HNO}_3$  was supplied by Risø National Laboratory for Sustainable Energy (Denmark). Standard solutions of uranium and thorium were purchased from NIST (Gaithersburg, MD).

Eichrom TEVA extraction chromatographic resin was purchased from TRISKEM International (Bruz, France). A metered amount of resin (100–150  $\mu\text{m}$  particle size) ranging from 0.65 to 0.70 g was swelled in water and loaded into a PMMA cylindrical column (5 mm diameter  $\times$  7 cm length) and preconditioned with  $\text{HNO}_3$  of identical concentration as the sample loading solution.

Three certified reference materials including soil (IAEA-375), sediment (IAEA-135), and seaweed (NIST-4359)<sup>32</sup> and two reference materials from a laboratory round-robin intercomparison, a Danish soil<sup>33</sup> and an Irish Sea sediment, were utilized for evaluation of method accuracy. Table S-1 of the Supporting Information lists detailed information concerning these reference materials along with three additional environmental samples, including seaweed, seawater, and soil, and an aqueous radionuclide cocktail (working solution) used in this work. Otherwise stated, the Danish soil was selected for method development.

**Sample Pretreatment.** A certain amount of a given sample (depending on the concentration of Pu), namely, 1–200 g of soil, sediment, or seaweed, and 200 L of seawater was spiked with 10 mBq  $^{242}\text{Pu}$  as a chemical yield tracer of the overall separation procedure. Detailed procedures for sample pretreatment can be found in the Supporting Information. In brief, after ashing of samples at 550  $^\circ\text{C}$  and acid leaching with aqua regia, Pu isotopes were coprecipitated with iron hydroxides and, thus, isolated from major components of the sample matrix. The precipitate was dissolved with  $\text{HCl}$ , and the redox pair  $\text{K}_2\text{S}_2\text{O}_5$ – $\text{NaNO}_2$  was used

for valence adjustment of the overall Pu to Pu(IV). The final sample solution was kept in 1.0 mol/L  $\text{HNO}_3$  prior to loading onto the column packed with TEVA resin.

**Automated Separation Scheme.** The SI-extraction chromatographic procedure consists of five steps as follows: (I) Rinsing of holding coil with 50 mL of deionized water and washing sample inlet and outlet tubing with 1.0 mol/L  $\text{HNO}_3$  at a flow rate of 10 mL/min followed by filling of sample tubing; (II) Loading the sample (from 14 to 280 mL, depending on the sample size, e.g., 14 mL for 10 g Danish soil) in a 1.0 mol/L  $\text{HNO}_3$  medium onto the TEVA column at 1.0 mL/min following sample aspiration into HC; (III) Rinsing of the column with 60 mL of 1.0 mol/L  $\text{HNO}_3$  to remove most of the uranium and matrix elements, followed by 60 mL of 9.0 mol/L  $\text{HCl}$  to remove thorium at 2.5 mL/min; (IV) Elution of Pu with 10 mL of 0.1 mol/L  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in a 2 mol/L  $\text{HCl}$  medium at 1.0 mL/min; (V) Cleaning of the column with 20 mL of 0.1 mol/L  $\text{NH}_2\text{OH}\cdot\text{HCl}$ –2 mol/L  $\text{HCl}$  followed by 60 mL of 0.1 mol/L  $\text{HCl}$  at 2.5 mL/min prior to loading of the next sample.

The 10 mL eluate was evaporated to dryness on a hot-plate following the addition of concentrated nitric acid and heating to decompose the hydroxylamine and eliminate the hydrochloric acid. The residue was dissolved in 5 mL of 0.5 mol/L  $\text{HNO}_3$  and the resulted solution was analyzed by ICP-MS for quantification of Pu isotopes and interfering nuclides.

**Investigation on the Separation Behavior of Pu, U, Th, and Am on TEVA Resin.** To investigate the separation behavior of different radionuclides on TEVA column, a working solution (radionuclides cocktail) containing about 0.1 Bq of  $^{242}\text{Pu}$ , 0.1 Bq of  $^{243}\text{Am}$ , 0.1 Bq of  $^{238}\text{U}$ , and 0.04 Bq of  $^{232}\text{Th}$  in 3 mL of 1.0 mol/L  $\text{HNO}_3$  was prepared and loaded onto the TEVA column. A total of 50 mL of 1 mol/L  $\text{HNO}_3$  and 15 mL of 9 mol/L  $\text{HCl}$  were consecutively applied as washing media for the column. Finally, Pu was eluted with 20 mL of 0.1 mol/L  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in a 2 mol/L  $\text{HCl}$  medium. Effluent, washes, and eluate were collected in 1.0–2.5 mL fractions and analyzed for  $^{242}\text{Pu}$ ,  $^{243}\text{Am}$ ,  $^{238}\text{U}$ , and  $^{232}\text{Th}$  using ICP-MS after reconstitution in 0.5 mol/L  $\text{HNO}_3$  and addition of In(III) as an internal standard (see below).

**Determination of Plutonium Isotopes Using ICP-MS.** To 5 mL of processed sample or leachate solution (diluted in 0.5 mol/L  $\text{HNO}_3$ ) was added 50  $\mu\text{L}$  of 100  $\mu\text{g/L}$  In(III) (as  $\text{InCl}_3$ ) as an internal standard. The concentrations of  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ , and  $^{242}\text{Pu}$ , as well as  $^{238}\text{U}$ ,  $^{232}\text{Th}$ ,  $^{200}\text{Hg}$ , and  $^{208}\text{Pb}$ , were determined by inductively coupled plasma-mass spectrometry (ICP-MS; X Series<sup>II</sup>, Thermo Fisher Scientific, Waltham, MA) equipped with an Xs-skimmer core and a concentric nebulizer under hot plasma conditions. The operational conditions of the instrument are listed in Table S-2.  $^{239}\text{Pu}$  standard solutions were prepared in 0.5 mol/L  $\text{HNO}_3$  containing 1.0  $\mu\text{g/L}$  In(III). The detection limits calculated as 3  $\sigma$  of processing blank were 1.5 pg/L for  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ , and  $^{242}\text{Pu}$ . A 0.5 mol/L  $\text{HNO}_3$  solution was used as a washing solution between consecutive assays. No carry-over effects were observed for consecutive analysis of samples differing up to 3 orders of magnitude in Pu concentration (see Results and Discussion). The regression line was proven to be linear over the range of 0.01 to 100 ng/L.

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## RESULTS AND DISCUSSION

**Valence Adjustment of Pu.** Among the different oxidation states of Pu, TEVA resin is merely suitable for the adsorption of tetravalent Pu in nitric acid medium because of the formation of anionic complexes of Pu with  $\text{NO}_3^-$ . Thus, the overall Pu in the sample has to be adjusted to Pu(IV). The most commonly exploited method are either one-step valence adjustment by resorting to  $\text{NaNO}_2$  or ascorbic acid<sup>26,34</sup> or two-step valence adjustment by the consecutive usage of reducing (e.g.,  $\text{K}_2\text{S}_2\text{O}_5$  or  $\text{Fe}(\text{NH}_2\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and oxidizing (e.g.,  $\text{NaNO}_2$ ) reagents.<sup>35–39</sup> In this work, three methods for valence adjustment were ascertained in regard to the operational time and chemical yield of Pu, as well as the decontamination factors for U, Th, Hg, and Pb, using 10 g of Danish soil as a model sample.

In the first method, the sample was loaded onto the TEVA column without any valence adjustment. In the second method, 200 mg of ascorbic acid were added to the sample solution (in 3 mol/L  $\text{HNO}_3$ ), and the solution was kept for 1 h to facilitate the conversion of Pu(III, V, and VI) to Pu(IV). From a thermodynamics viewpoint, ascorbic acid can reduce all Pu to Pu(III),<sup>40,41</sup> and under the presence of Fe, the reaction can be speeded up.<sup>34</sup> Because of the instability of Pu(III) and the unavoidable existence of nitrite in ascorbic acid- $\text{HNO}_3$  medium, Pu(III) might be oxidized to Pu(IV) within a short time frame. In the third method, 300 mg of  $\text{K}_2\text{S}_2\text{O}_5$  was added to the Fe containing sample (in 3 mol/L  $\text{HNO}_3$ ) and stirred for 20 min at room temperature to reduce the overall Pu to Pu(III). Thereafter, the solution pH was adjusted to 9 to coprecipitate Pu(III) with  $\text{Fe}(\text{OH})_2$ . The coprecipitate was dissolved in 10 mL of 4 mol/L  $\text{HNO}_3$ , whereupon 100 mg of  $\text{NaNO}_2$  was added to oxidize Pu(III) to Pu(IV). To eliminate the nitrogen oxides generated during Pu oxidation, the sample was heated on a hot plate at 120 °C for 5 min.

The results (Table S-3) show a very low chemical yield of Pu (<35%) in the first method, which indicates the presence of mixed oxidation states of Pu (e.g., Pu(IV, V, and VI)) in the sample medium. On the contrary, chemical yields of Pu in the other two methods were in the range of 95–103%. It should be, however, borne in mind that the chemical valence adjustment using ascorbic acid is greatly dependent upon the amount of ascorbic acid, Fe, and  $\text{HNO}_3$  in the final sample solution as well as on the reaction temperature, which affects the concentration of nitrite and the oxidation of ascorbic acid. Accordingly, the chemical yields of Pu might be subjected to variation according to the experimental conditions selected. In addition, the reaction time and decontamination factors for  $^{238}\text{U}$ , Hg, and Pb using  $\text{K}_2\text{S}_2\text{O}_5$ – $\text{NaNO}_2$  were superior to those of the ascorbic acid method. Particularly relevant is the 4-fold improved decon-

tamination factor for  $^{238}\text{U}$ , which might seriously interfere in the ICP-MS quantification of  $^{239}\text{Pu}$ .

One-step valence adjustment using  $\text{NaNO}_2$  has been proposed by Montero et al.<sup>37</sup> However, low chemical yields of Pu (~40%) were obtained in their work. In principle,  $\text{NaNO}_2$  can reduce Pu(VI) to Pu(IV) and oxidize Pu(III) to Pu(IV) in  $\text{HNO}_3$ , thus, it is conceivable to adjust all Pu to Pu(IV). Yet, the reduction of Pu(VI) to Pu(IV) actually needs several hours under room temperature and moderate concentrations of  $\text{HNO}_3$  for completion if no catalyst is added.<sup>42</sup> With the addition of Fe(II), the reduction of Pu(VI) to Pu(IV) can be promoted.<sup>42</sup> However, the reduction of Pu(VI) to Pu(IV) in environmental samples might still not be fast enough to be completed within a reasonable time frame due to the low level of Pu contained in the samples. In this case, the Pu(VI) fraction, which is not converted into Pu(IV), is to be lost during the separation with TEVA column. The most suitable procedure for quantitative valence adjustment is thus the reduction of Pu to Pu(III), with a strong reductant followed by oxidation of the resulting Pu(III) to Pu(IV) by nitrite, that is, via a two-step valence adjustment. This procedure is generally fast enough to convert the overall Pu into Pu(IV) in a few minutes.<sup>42</sup> Therefore, a two-step valence adjustment using the redox pair  $\text{K}_2\text{S}_2\text{O}_5$ – $\text{NaNO}_2$  was ultimately chosen for valence adjustment in the present work.

**Separation Procedure. Removal of Interferences.** U, Th, Hg, and Pb are naturally abundant elements in most of environmental samples including soil and sediment. Large amounts of  $^{238}\text{U}$  and isotopes of Hg and Pb might prevent accurate quantification of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  by ICP-MS because of isobaric interferences of polyatomic ions  $^{238}\text{U}^1\text{H}$ ,  $^{238}\text{U}^2\text{H}$ ,  $^{202}\text{Hg}^{37}\text{Cl}$ ,  $^{200}\text{Hg}^{40}\text{Ar}$ ,  $^{208}\text{Pb}^{31}\text{P}$ ,  $^{204}\text{Pb}^{35}\text{Cl}$ ,  $^{206}\text{Pb}^{33}\text{S}$ , and tailing of  $^{238}\text{U}$  in 239 mass region. In addition,  $^{241}\text{Am}$  and Th isotopes would interfere with the eventual detection of Pu isotopes by alpha spectrometry ( $^{241}\text{Am}$  to  $^{238}\text{Pu}$ , and  $^{229}\text{Th}$  and  $^{230}\text{Th}$  to  $^{242}\text{Pu}$ ). According to the elution profiles on the TEVA column, strong sorption of Pu was observed in 1–3 mol/L  $\text{HNO}_3$ , while U along with most of matrix elements, for example, Hg and Pb, were eluted at a large extent during the sample loading and rinsing with  $\text{HNO}_3$  (see Figure 2). Moreover, Th is readily stripped out from the column in a 6–9 mol/L  $\text{HCl}$  medium without significant elution of Pu. To improve the decontamination factors of these potentially interfering elements, different chromatographic separation conditions, including the concentration and the volume of washing solutions and flow rates, were investigated for the determination of Pu in the Danish soil.

Experimental results (see Table S-4) demonstrated that the larger was the volume of rinsing solution, the better were the decontamination factors for U, Pb and Hg. 1.0 mol/L  $\text{HNO}_3$  was proven to be the most effective reagent for both sample loading and the first rinsing step, which is in good agreement with previously published works.<sup>26,43</sup> In fact, decontamination factors of  $>10^5$  for U were encountered when rinsing the column with 60 mL of 1.0 mol/L  $\text{HNO}_3$  (see groups 9–11 in Table S-4). In addition, to avoid the potential introduction and remaining of uranium onto the column during  $\text{HCl}$  rinsing (U as impurity in

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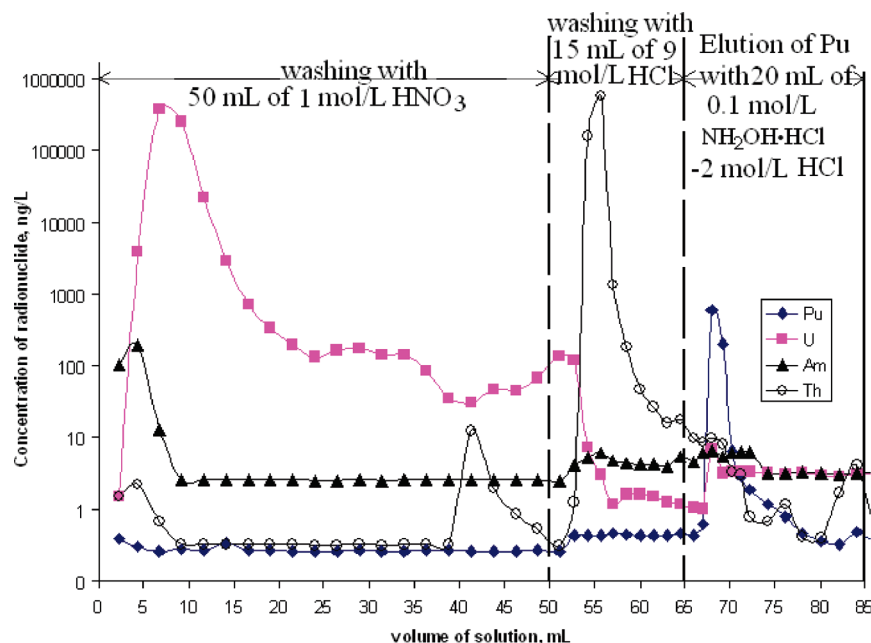
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**Figure 2.** Sorption and elution behavior of Pu, U, Th, and Am in the SI-extraction chromatographic system furnished with a TEVA resin packed column

HCl reagent), the  $\text{HNO}_3$  rinsing was split into a first step of 40 mL before the HCl rinsing and 20 mL afterward. However, no significant improvement on the decontamination of U was observed. This implies that uranium in HCl solution as impurity is not significant. Therefore, one-step rinsing with 1–3 mol/L  $\text{HNO}_3$  suffices for sufficient removal of large amounts of U.

Different options for further column rinsing by resorting to concentrated HCl were investigated for the efficient removal of Th. Experimental results (Table S-4) revealed that a decontamination factor of  $>10^4$  for  $^{232}\text{Th}$  was obtained when using 50–60 mL of solution composed of 6 or 9 mol/L HCl following the  $\text{HNO}_3$  washing (see groups 8–11 in Table S-4). Finally, a 9 mol/L HCl solution was adopted for the removal of Th, which is in good agreement with earlier findings.<sup>34,44,45</sup>

Flow rates for sample cleanup were varied within the range of 1.0 to 5.0 mL/min (see groups 7, 8, and 12 in Table 2) aimed at increasing the sample throughput and, thus, improving the analytical efficiency without significant deterioration of the separation efficiency and the chemical yield for target radionuclides. At 5.0 mL/min the chemical yield of Pu and the decontamination factors for U, Th, Hg, and Pb are still acceptable, yet, because of the increase of the backpressure observed in the SI-column system, the washing flow rate was affixed to 2.5 mL/min for the remainder of the work. The sample loading flow rate was however set to 1.0 mL/min to ensure quantitative uptake of Pu as demonstrated by the results of chemical yields of  $^{242}\text{Pu}$  compiled in Table S-4.

**Elution of Plutonium.** A variety of eluents for the elution of Pu from TEVA resin have been reported including diluted  $\text{HF-HNO}_3$  solution,<sup>7,8</sup> diluted  $\text{HF-HCl}$  solution,<sup>43</sup> 0.5 mol/L HCl,<sup>6</sup> 0.1 mol/L  $\text{H}_2\text{C}_2\text{O}_4$ –0.05 mol/L  $\text{HNO}_3$ ,<sup>45</sup> 0.01 mol/L  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ ,<sup>24</sup> and 0.1% hydroxyethylidene diphosphonic acid.<sup>9</sup> Earlier research-

ers demonstrated that Pu can be efficiently eluted from TEVA resin by a reducing solution (e.g., hydroxylamine hydrochloride) in diluted acid media as a result of the reduction of Pu to Pu(III).<sup>46,47</sup> Because of the eventual concomitant presence of residual amounts of Pb and Hg onto the column, and the formation of polyatomic molecules, such as  $^{204}\text{Pb}^{35}\text{Cl}$ ,  $^{204}\text{Hg}^{35}\text{Cl}$ , and  $^{202}\text{Hg}^{37}\text{Cl}$  in a HCl medium, an eluent composed of 0.1 mol/L  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 0.1 mol/L  $\text{HNO}_3$  was assessed as an eluting medium for Pu to facilitate direct injection into ICP-MS. However, experimental results (see groups 2–4 in Table S-4) indicates distinctly lower decontamination factors for  $^{238}\text{U}$  ( $<10^3$ ) as compared to 10–100-fold improved decontamination ( $10^4$ – $10^5$ ) when using the same concentration of hydroxylamine in 2 mol/L HCl. This is most likely a consequence of the low distribution constants of uranium onto TEVA resin in diluted nitric acid solutions, whereby the remainder of U onto the resin coeluted with Pu.<sup>33</sup> Accordingly, 0.1 mol/L  $\text{NH}_2\text{OH}\cdot\text{HCl}$ –2 mol/L HCl was selected as eluent for Pu in this work.

Pu isotopes were quantitatively eluted at 1.0 mL/min flow rate in the first 10 mL of eluate with chemical yields  $>90\%$ . Yet, direct injection of the eluate into ICP-MS rendered 2-fold decreased efficiency for Pu with respect to that of a standard solution in 0.5 mol/L  $\text{HNO}_3$  medium (see Table S-5 for further details) as a consequence of the high concentration of chloride ions in the eluate. Therefore, wherever off-line detection was conducted, the eluate was first evaporated to dryness and reconstituted in 0.5 mol/L  $\text{HNO}_3$  as detailed in the Experimental Section to improve the detection sensitivity and reduce the risk of generation of polyatomic interfering species.

**Reusability of TEVA Resin and Carryover Effects.** The potential reusability of the TEVA resin is crucial for the development of a fully automated and cost-effective SI-extraction chro-

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**Table 1. Evaluation of the Analytical Performance of a Single TEVA Column Utilized in Repetitive Assays<sup>a</sup>**

sample number	addition of <sup>239</sup> Pu (mBq)	chemical yield ( <sup>242</sup> Pu; %)	<sup>239</sup> Pu measured		decontamination factor		
			(mBq)	(%) <sup>b</sup>	<sup>238</sup> U	<sup>232</sup> Th	<sup>208</sup> Pb
1	6.13	95.4	8.01	106.4	5.7 × 10 <sup>4</sup>	2.1 × 10 <sup>4</sup>	1.4 × 10 <sup>4</sup>
2	0.00	99.8	1.40	100.0	2.2 × 10 <sup>4</sup>	2.9 × 10 <sup>4</sup>	4.2 × 10 <sup>4</sup>
3	23.07	100.0	23.06	94.2	1.6 × 10 <sup>4</sup>	2.5 × 10 <sup>4</sup>	2.7 × 10 <sup>4</sup>
4	5.84	100.0	7.50	103.6	1.9 × 10 <sup>4</sup>	2.4 × 10 <sup>4</sup>	5.2 × 10 <sup>3</sup>
5	0.00	95.8	1.68	120.0	2.6 × 10 <sup>4</sup>	2.2 × 10 <sup>4</sup>	3.1 × 10 <sup>4</sup>
6	21.04	104.3	22.22	99.0	9.5 × 10 <sup>3</sup>	1.5 × 10 <sup>4</sup>	4.9 × 10 <sup>3</sup>
7	5.36	100.0	6.78	100.3	3.4 × 10 <sup>4</sup>	2.1 × 10 <sup>4</sup>	1.3 × 10 <sup>4</sup>
8	0.00	100.0	1.47	105.0	1.0 × 10 <sup>5</sup>	2.3 × 10 <sup>4</sup>	3.8 × 10 <sup>4</sup>
9	20.43	104.6	22.86	104.7	7.2 × 10 <sup>4</sup>	2.1 × 10 <sup>4</sup>	3.6 × 10 <sup>4</sup>
10	4.87	100.0	5.96	95.1	1.2 × 10 <sup>5</sup>	1.3 × 10 <sup>4</sup>	1.8 × 10 <sup>4</sup>
11	0.00	100.0	1.42	101.4	1.2 × 10 <sup>5</sup>	5.8 × 10 <sup>3</sup>	3.3 × 10 <sup>4</sup>
12	23.52	100.0	23.43	94.0	1.3 × 10 <sup>5</sup>	1.0 × 10 <sup>4</sup>	2.8 × 10 <sup>4</sup>
13	5.23	100.0	6.55	98.8	1.7 × 10 <sup>5</sup>	1.0 × 10 <sup>4</sup>	2.6 × 10 <sup>4</sup>
14	0.00	100.5	1.44	102.9	1.6 × 10 <sup>5</sup>	4.9 × 10 <sup>3</sup>	6.7 × 10 <sup>3</sup>
15	20.48	103.9	22.11	101.1	4.0 × 10 <sup>4</sup>	8.8 × 10 <sup>3</sup>	1.2 × 10 <sup>4</sup>
16	0.00	100.0	1.44	102.9	2.1 × 10 <sup>5</sup>	7.3 × 10 <sup>3</sup>	1.7 × 10 <sup>4</sup>
17	22.28	100.0	23.72	100.2	4.3 × 10 <sup>4</sup>	6.7 × 10 <sup>3</sup>	5.0 × 10 <sup>3</sup>
18	5.56	98.1	6.79	97.6	3.0 × 10 <sup>5</sup>	1.2 × 10 <sup>4</sup>	2.9 × 10 <sup>4</sup>
19	20.27	100.0	18.74	86.5	1.9 × 10 <sup>4</sup>	2.2 × 10 <sup>3</sup>	4.1 × 10 <sup>3</sup>
20	5.71	94.8	7.43	104.5	6.5 × 10 <sup>4</sup>	1.7 × 10 <sup>3</sup>	3.0 × 10 <sup>3</sup>
average (±SD)		99.9 ±2.6			6.4 × 10 <sup>4</sup>	1.6 × 10 <sup>4</sup>	2.0 × 10 <sup>4</sup>

<sup>a</sup> The reported <sup>239</sup>Pu concentration in the Danish soil sample is 0.140 ± 0.008 mBq/g, the total <sup>239</sup>Pu in 10 g of sample is 1.40 ± 0.08 mBq. The uncertainties of the chemical yield measured by <sup>242</sup>Pu and <sup>239</sup>Pu activity are <3% and <4%, respectively, and the uncertainty of decontamination factors for U, Th, and Pb are lower than 10%. <sup>b</sup> Percentages are given as the ratio of the activity of <sup>239</sup>Pu measured by ICP-MS (mBq) and the sum of the total activity of <sup>239</sup>Pu (mBq) in the spiked sample.

matographic method for continuous and rapid analysis of a large number of samples. The extended use of the resin might lead to the deterioration of resin performance due to its eventual contamination by matrix ingredients, the undue build-up backpressure and the loss of the aliphatic quaternary amine immobilized on the resin, which in turn would rise to impaired separation efficiency. Sample cross-contamination (carryover effects) is another important issue to cope with whenever samples with significant different levels of Pu are to be analyzed. The potential reuse of the TEVA column as a permanent and integral unit within the SI manifold was investigated on account of the long-term data on chemical yields of Pu, decontamination factors of interferences, as well as carryover effects.

To investigate sample cross-contamination, two Danish soil samples (10 g each) spiked with about 30 or 40 mBq of <sup>242</sup>Pu and about 60 mBq of <sup>239</sup>Pu and 6 blank samples (1.0 mol/L HNO<sub>3</sub>) were consecutively analyzed using a single TEVA packed column in the order given in Table S-6. After elution, the column was rinsed two or three times with 10 mL of 0.1 mol/L NH<sub>2</sub>OH·HCl–2 mol/L HCl and each eluate/rinse solution was collected for the determination of Pu. Between samples, 60 mL of 0.1 mol/L HCl was used to remove any possible remains of U, Th, Pu, and other interferences on the column. Analyte carryover (in percentage) was calculated as the ratio of Pu activity in a given effluent to that of the spiked sample. Experimental results in Table S-6 indicate that although 1.0–1.3% of Pu was observed in the second 10 mL of eluate, this effect is reduced to <0.1% in the next sample after rinsing with 20–30 mL of eluent and 60 mL of 0.1 mol/L HCl, whereby the cross-contamination (carryover) between samples can be neglected in the proposed setup. It has been earlier reported that diluted HF

can efficiently remove Pu from the TEVA column.<sup>7,48</sup> Hence, an additional elution of the column with 0.1 mol/L HF was conducted after 3 × 10 mL of 0.1 mol/L NH<sub>2</sub>OH·HCl–2 mol/L HCl eluent. Yet, no measurable amounts of Pu were found in the eluate of 0.1 mol/L HF (see Table S-6). It is therefore possible to conclude that 30 mL of 0.1 mol/L NH<sub>2</sub>OH·HCl–2 mol/L HCl elution suffices for quantitative stripping out of Pu, and that an excessively long elution protocol with HF is not necessary.

Aiming at investigating the potential reusability of a packed TEVA column in the SI manifold, 40 Danish soil samples (10 g of each) were prepared, spiked with a given amount of <sup>239</sup>Pu (0–24 mBq) and <sup>242</sup>Pu tracer, and consecutively analyzed using a single column containing about 0.70 g of TEVA resin (see Table 1). The chemical yields of Pu (monitored by <sup>242</sup>Pu) for the first 20 samples were within the range of 95–105%, which indicates the feasibility of implementation of a permanent TEVA column in the flow network for repetitive sample analyses. Previously, up to nine consecutive uses of a TEVA column in an SI system has been reported by Kim et al.<sup>34</sup> for the simultaneous determination of Np and Pu. Actually, our experimental results showed that the sample column could be reused for up to about forty times (see Table S-7 in the Supporting Information), but after 20-fold runs, an increased flow backpressure was eventually observed. In general, the activity of <sup>239</sup>Pu determined in the first twenty samples was in good agreement with the expected value (activity in the sample plus spikes). A disagreement for the last 4 out of 40 samples (Nos. 37–40 in Table S-7) was however detected, which was attributed to a column leakage effect. Notwithstanding the fact that decontamination factors for <sup>238</sup>U, <sup>232</sup>Th, and Pb decreased slightly with the reuse of the resin,

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**Table 2. Investigation of the Separation Capability of the SI-TEVA System<sup>a</sup>**

sample amount (g; Danish soil)	chemical yield ( <sup>242</sup> Pu; %)	<sup>239+240</sup> Pu measured (Bq/kg)	decontamination factor		
			<sup>238</sup> U	<sup>232</sup> Th	<sup>208</sup> Pb
10	97.4 ± 4.5	0.25 ± 0.01	1.1 × 10 <sup>5</sup>	1.5 × 10 <sup>4</sup>	1.9 × 10 <sup>4</sup>
100	77.0 ± 12.6	0.27 ± 0.03	3.8 × 10 <sup>4</sup>	1.9 × 10 <sup>3</sup>	1.2 × 10 <sup>4</sup>
200	69.3 ± 22.6	0.23 ± 0.03	1.2 × 10 <sup>4</sup>	1.4 × 10 <sup>3</sup>	2.8 × 10 <sup>3</sup>

<sup>a</sup> The reported <sup>239+240</sup>Pu concentration in the Danish soil is 0.238 ± 0.014 Bq/kg. Results are given as the average of three replicates ± standard deviation.

average values of  $6.4 \times 10^4$ ,  $1.6 \times 10^4$ , and  $2.0 \times 10^4$  were obtained for <sup>238</sup>U, <sup>232</sup>Th, and Pb, respectively, which suffice for accurate determination of Pu in environmental samples. As can be seen from Table 1, the decontamination factors in the different experiments are rather variable. For the most important interfering element, U, the decontamination factor varies about 10-fold among samples. The amount of U in the purified samples is within the nanogram or subnanogram range, whereby the contribution from laboratory glassware and other equipment becomes significant. Pb, in particular, has been shown to be notoriously difficult to completely remove due to its overall presence. The variation of decontamination factors of Pb in Table 1 to some extent reflects the variation of Pb contamination in the washing solutions, eluent, detection instrument, and auxiliary equipment.

**Separation Capability of the SI-TEVA Method for Environmental Assays.** Several extraction chromatographic flow-based methods have been reported in the literature for the determination of Pu in environmental and waste samples, yet no methods for analysis of solid samples (soil/sediment) using more than 4 g are available to date.<sup>23,26,28,30</sup> The concentrations of Pu isotopes in environmental samples range widely according to the sample location and sources of plutonium. For example, accurate analysis of samples with <sup>240</sup>Pu concentration lower than 1 mBq/kg (ca. 0.1 fg/g), for example, deep soil exposed to nuclear weapon testing fallout, requires more than 100 g samples whether alpha spectrometry or ICP-MS is used for quantification. However, the handling of large sized samples for determination of trace levels of Pu in a small column might lead to insufficient removal of interferences (low decontamination factors) and/or significantly decreased chemical yields for Pu.

To examine the reliability of the SI-TEVA system for handling large sample volumes, the dependence of the separation efficiency upon the amount of Danish soil processed (from 10 to 200 g, with sample loading volumes ranging from 14 to 280 mL) was assessed. Despite the decrease of chemical yields from 97 to 69% when increasing the soil amount from 10 to 200 g, and the slight diminution of decontamination factors for U and Pb when handling 100–200 g soil, the performance of the separation system for up to 200 g of soil is still satisfactory for accurate determination of low levels of Pu (Table 2). The concentration of <sup>239+240</sup>Pu determined in 200 g of soil (namely, 0.23 ± 0.03 Bq/kg) is in very good agreement with the reference value (0.238 ± 0.014 Bq/kg). Therefore, the proposed SI-based analytical method using a downscaled TEVA extraction chromatographic column should be regarded as an appealing approach for the automation of separation protocols for Pu at environmentally relevant levels.

**Method Validation and Analytical Applications.** To assess the accuracy and applicability of the proposed analytical method for handling environmental samples with different levels of Pu and of variable matrix complexity, three standard reference materials including IAEA-375 soil (5 g), IAEA-135 sediment (0.5 g), NIST-4359 seaweed (20 g), and two reference samples, an Irish Sea Sediment (1 g) and a Thule soil (1 g; see Table S-1 for further information), were analyzed. The concentration of Pu in two additional environmental samples, namely, a seaweed (20 g) from Danish coast and seawater (200 L) from the Nordic Sea, were also analyzed. The analytical results of <sup>239</sup>Pu and <sup>240</sup>Pu for the overall reference materials and real samples (compiled in Table 3) agree very well with the certified (or reference) values or those values reported by earlier researchers<sup>46</sup> or determined by anion exchange chromatography and alpha spectrometry. As shown in Table S-8,  $t_{\text{exp}}$  values were in all instances lower than the  $t_{\text{crit}}$  at the 0.05 significance level, which revealed the inexistence of significant differences between experimental and certified concentrations of Pu for the overall materials.

The SI-extraction chromatographic separation takes about 1.5 h per sample. Thus, the automated setup is capable of handling up to 16 samples within one day. Compared with the traditional manual methods, the separation efficiency is here 20–30 fold improved.<sup>4,39</sup> The proposed method is therefore better suited for the rapid determination of Pu isotopes as endorsed in environmental risk assessment and radiological emergencies. Besides the satisfactory recoveries of analytes, appropriate decontamination factors for interferences, and the wide applicability to distinct environmental samples (viz., soil, sediment, plant tissues, seawater) with good accuracy, the robust SI system herein proposed operated continuously for a long time frame (up to 8 months had already been confirmed) without any serious problem, like software shutdown. In addition, the maintainance of the system is also very simple and cost-effective.

## CONCLUSION AND PERSPECTIVE

In this paper, an automated SI-TEVA extraction chromatographic method has been proposed as an appealing alternative to tedious batch-wise extraction procedures for rapid determination of Pu isotopes in environmental samples at trace levels. The SI setup features unique attributes detailed as follows: (I) A single chromatographic column could be reused for at least 20 assays with minimum operational maintenance; (II) 16 samples can be handled in one day using a single setup; (III) Large size samples,

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**Table 3. Determination of Pu Isotopes in Reference Materials and Environmental Samples Exploiting SI-TEVA Extraction Chromatography and Detection by ICP-MS<sup>a</sup>**

sample	<sup>239</sup> Pu spiked (Bq/kg)	chemical yield (%)	<sup>239</sup> Pu measured (Bq/kg)	<sup>240</sup> Pu measured (Bq/kg)	<sup>239+240</sup> Pu measured (Bq/kg)	reference activity of Pu isotopes <sup>b</sup> (Bq/kg)		
						<sup>239</sup> Pu	<sup>240</sup> Pu	<sup>239</sup> + <sup>240</sup> Pu
IEAE-375 soil	0	84.4 ± 10.2	0.14 ± 0.02	0.16 ± 0.02	0.30 ± 0.02	0.113 ± 0.010 <sup>c</sup>	0.124 ± 0.020 <sup>c</sup>	0.30 (0.26 ± 0.34)
IAEA-135 sediment	0	79.7 ± 7.6	126.2 ± 4.5	93.8 ± 3.6	220.0 ± 7.9	123.0 ± 3.8 <sup>d</sup>	93.8 ± 2.3 <sup>d</sup>	213 (205 ± 226)
Irish Sea sediment	0	85.7 ± 15.9	225.9 ± 6.2	201.3 ± 54.9	427.2 ± 56.6	237.0 ± 5.0 <sup>d</sup>	181.0 ± 4.9 <sup>d</sup>	419.0 ± 10.6
Thule soil	0	80.0 ± 10.5	1.46 ± 0.06	0.38 ± 0.08	1.84 ± 0.09	-	-	1.87 ± 0.17 <sup>e</sup>
Danish soil	0	91.6 ± 14.5	0.14 ± 0.01	0.09 ± 0.02	0.23 ± 0.03	0.140 ± 0.008	0.098 ± 0.006	0.238 ± 0.014
seaweed	0.61 ± 0.01	87.9 ± 16.7	0.61 ± 0.02	0.02 ± 0.01	0.63 ± 0.03			
seaweed	0	89.3 ± 13.7	0.03 ± 0.01	0.01 ± 0.01	0.04 ± 0.01			
seawater <sup>g</sup>	0	67.7 ± 7.9	3.9 ± 0.5	2.9 ± 0.1	7.8 ± 0.5			7.1 ± 0.7 <sup>f</sup>

<sup>a</sup> Results are given as the average of three replicates ± standard deviation. <sup>b</sup> Certified values for standard reference materials or reference values for interlaboratory round-robin comparison samples (Danish Soil, Irish Sea sediment); <sup>c</sup> Literature value;<sup>49</sup> <sup>d</sup> Literature value;<sup>46</sup> <sup>e</sup> Separated by anion exchange chromatography and detected by α-spectrometry; <sup>f</sup> Detected by α-spectrometry. <sup>g</sup> Concentrations given in Bq/L.

for example, up to 200 g of soil or sediment and 200 L of seawater can be processed with minimum deterioration of the separation efficiency; (IV) Environmental samples, for example, soil, sediment, plants tissues, and seawater, with variable matrix ingredients and different levels of Pu, could be treated in a single SI manifold with no need for system reconfiguration; (V) Samples are handled in an entirely enclosed setup. This in turn would lead to enhanced operator safety in the determination of radionuclides with minimum risks of sample contamination. The proposed SI-based method, thus, meets the requirements set in environmental radiation monitoring, radioecological studies, and emergency preparedness programs.

The detection of Pu isotopes by ICP-MS can be conducted in a fully automated fashion, in which case the external selection valve SV-3 is replaced with a 'Y-type' connector for online introduction of the eluate and internal standard into the ICP-MS, and a trigger for activating the operation of ICP-MS instrument should be utilized. In our analytical system, we did not hyphenate

the SI setup with ICP-MS because of the larger consumption of Ar gas, lower detection limits, and the occurrence of isobaric interferences from the HCl eluate medium.

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## SUPPORTING INFORMATION AVAILABLE

Additional information as noted in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## SUPPORTING INFORMATION

### **Rapid Determination of Plutonium Isotopes in Environmental Samples Using Sequential Injection Extraction Chromatography and Detection by inductively Coupled Plasma Mass Spectrometry**

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This Supporting Information described the details on samples and sample pre-treatment. It also includes 7 Tables and 1 Figure, and in total 12 pages.

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## Experimental

### Samples

A Danish soil (NKS inter-comparison sample in Nordic labs for environmental radioactivity) was collected from top 10 cm and at 12 different Danish locations in 2003. The samples pooled and mixed at Risø-DTU, Denmark. The dried soil was ground and sieved through a 0.4 mm sieve<sup>1</sup>. This soil has been analyzed for radionuclides including Pu isotopes by 10 laboratories during a Nordic round robin inter-comparison, and the reference values for radionuclides have been endorsed. An Irish Sea sediment was collected from the British coast in the Irish Sea, at a location of 15 km far from the Sellafield reprocessing plant, and was freeze-dried and sieved through a 0.4 mm sieve<sup>2</sup>. One soil sample was collected from 7.5-10 cm top in Thule, Greenland (76°27.283N, 69°15.355W) in 2003, where Pu isotopes are expected to be found because of the nuclear weapon accident in 1968. Environmental samples with low levels of Pu, namely a surface-water from North Sea and a seaweed sample (*Fucus vesiculosus*) were also analysed. The latter was collected from the Klint, Danish coast in the Kattegat in July 2003. The sample was first air dried followed by oven-drying at 70-80 °C for 2 days, then ground and sieved through a 0.4 mm sieve.

Several certified/standard reference materials were analysed in this work for method validation, which include IAEA-375 (a soil from Novozybkov, Brjansk, Russia), IAEA-135 (a sediment from Lune Estuary, UK) and an NIST seaweed (a blend of *Fucus vesiculosus*, *Laminaria saccharia* and *Ascophyllum nodosum*). The NIST seaweed was prepared as mixed seaweed samples collected from the western coast of Ireland and the White Sea. The collected seaweed was first air-dried, blade-milled and sieved, and then freeze-dried to a residual moisture below 5%<sup>3</sup>.

### Sample pre-treatment

For the analysis of soil, sediment and seaweed, sample pre-treatment was conducted before the chemical separation procedure. A certain amount of sample (1-200 g, depending on the concentration of Pu) was weighted in a beaker and ashed at 550°C overnight to decompose the organic matter. About 10 mBq of <sup>242</sup>Pu was spiked into the sample as a chemical yield tracer. The sample was then digested with *Aqua regia* on a hotplate at 150°C for 30 min and then 200 °C for 2 h. The beaker was covered with a glass-watch to prevent significant evaporation of the acid solution. After cooling, water was added and the sample was filtered through a GF/A filter (glass microfiber filters, 125 mm ø, Whatman International Ltd, Maidstone, England) and the filtrate was



directly collected into a centrifuge tube. The beaker and the filter were gently washed with 30 mL of 0.2 mol/L HCl.  $\text{NH}_4\text{OH}$  was added to the filtrate to adjust the pH at 8-9 and co-precipitate the plutonium with  $\text{Fe}(\text{OH})_3$  (for seaweed, a certain amount of  $\text{FeCl}_3$  was added to the sample prior to precipitation) and to remove Ca and Mg ions. The precipitate was separated by centrifugation. 6 mol/L of NaOH was added to the precipitate to remove the amphoteric elements, e.g. Al. The precipitate was dissolved with HCl, whereupon 300 mg of  $\text{K}_2\text{S}_2\text{O}_5$  were added, and the solution was stirred for 10 min to reduce the overall Pu to Pu(III) (along with the reduction of the overall Fe to Fe(II)). NaOH was added to the solution to adjust pH to 10 to co-precipitate Pu(III) with  $\text{Fe}(\text{OH})_2$ . The precipitate thus obtained was separated by centrifugation and then dissolved with a given volume of 1.0 mol/L  $\text{HNO}_3$  depending on the amount of  $\text{Fe}(\text{OH})_2$ . Before sample loading onto TEVA column, 100 mg of  $\text{NaNO}_2$  was added to oxidize Pu(III) to Pu(IV).

For seawater analysis, a certain volume of sample (~ 200 L) was placed in a container and acidified to pH 2 with concentrated HCl to prevent the adsorption of Pu on the wall of the container. To the acidified sample, 10 mBq of  $^{242}\text{Pu}$  as a chemical yield tracer, 2 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 100 g of  $\text{K}_2\text{S}_2\text{O}_5$  were added and stirred for 1h to reduce all Pu to Pu(III). Then, 6 mol/L NaOH was added to adjust the pH to 10. Pu(III) co-precipitated with  $\text{Fe}(\text{OH})_2$  in  $\geq 5\text{h}$ , and the supernatant was siphoned off. The precipitate, which contains Pu,  $\text{Fe}(\text{OH})_2$ , as well as the hydroxides and carbonates of other metals including Mg, Al, and Ca, was dissolved using concentrated HCl up to a final concentration of about 0.1 mol/L HCl. In addition, organic colloids carrying Pu might be associated to the precipitate and separated from the solution. 6%  $\text{NH}_4\text{OH}$  solution was slowly added to the solution to adjust the pH to 9-10 to co-precipitate Pu with  $\text{Fe}(\text{OH})_2$  and to remove most of the Ca, Mg, and some metals. The resulting precipitate was dissolved in 50 mL of concentrated HCl and 50 mL of concentrated  $\text{HNO}_3$  in a beaker and the solution was digested under heating and reflux on a hot-plate (180-200 °C) for 1-2 h to decompose the possible organic matters. After cooling, the solution was filtered through a GF/A filter, the filtrate was collected into a centrifuge tube and the filter was washed with 30 mL of 0.2 mol/L HCl.  $\text{NH}_4\text{OH}$  was added to the supernatant to adjust the pH at 8-9 to co-precipitate the plutonium with  $\text{Fe}(\text{OH})_3$ . The precipitate was separated by centrifugation. 6 mol/L of NaOH was added to remove the amphoteric elements. The precipitate was dissolved with HCl, whereupon 300 mg of  $\text{K}_2\text{S}_2\text{O}_5$  was added, and the solution was stirred for 10 min to reduce the overall Pu to Pu(III). NaOH was added to the solution to adjust the solution pH to 10, and the precipitate obtained was separated by centrifugation and then dissolved with a certain volume of 1.0 mol/L  $\text{HNO}_3$ . Pu(III) was finally converted into Pu(IV) by  $\text{NaNO}_2$  as described above.

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Table S-1. Characteristics and composition of samples analyzed throughout this work

Sample	Sample amount	Description	Sampling location
Artificial sample (working solution or radionuclides cocktail)	3 mL	Composition: 0.1 Bq of $^{242}\text{Pu}$ , 0.1 Bq of $^{243}\text{Am}$ , 0.1 Bq of $^{238}\text{U}$ and 0.04 Bq of $^{232}\text{Th}$ in 3 mL of 3 mol/L $\text{HNO}_3$ solution	Prepared in the lab
Danish soil (NKS inter-comparison sample)	10-200 g	Low-level environmental soil	The top 10 cm of 2mm sieved soil from 12 different Danish locations collected in 2003
IAEA-375 (soil)	5 g	Low-level contaminated soil	Obtained from the 'Staryi Viskov' collective farm in Novozybkov, Brjansk, Russia in July 1990
IAEA-135 (sediment)	0.5 g	Contaminated sediment	Sediment from the Lune Estuary, UK influenced by radioactive discharges from the Sellafield nuclear facility collected in 1991
Irish Sea Sediment	1 g	Contaminated sediment	Surface sediment from Irish Sea
Thule soil	1 g	Contaminated soil	Surface soil from Thule, Greenland, collected in 2003
NIST-4359 (seaweed)	20 g	A blend of <i>Fucus vesiculosus</i> , <i>Laminaria saccharia</i> and <i>Ascophyllum nodosum</i>	Collected from the western coast of Ireland and from the White Sea
Seaweed sample	20 g	<i>Fucus vesiculosus</i>	Collected from the Klint, Danish coast in the Kattegat in 2003
Seawater sample	200 L	Environmental seawater	Collected from North Sea in 2008

Table S-2. Selected operational conditions for ICP-MS detection of radionuclides

Forward power (W)	1400						
<i>Gas flow (L/min)</i>							
Coolant	13.8						
Auxiliary	0.80						
Nebuliser	1.03						
<i>Operation pressures (mbar)</i>							
Expansion	1.5 - 2.5						
Analysis	$5.3 \times 10^{-8}$						
Sample uptake rate (mL/min)	0.3						
Number of replicate runs	3						
Typical $^{238}\text{U}^1\text{H}/^{238}\text{U}$ ratio	$5 \times 10^{-5}$						
Typical plutonium sensitivity (cps/ppt)	200-400						
Typical uranium sensitivity (cps/ppt)	200-400						
Typical background at mass 239, 240 and 242 (cps)	0.6-1.0						
<i>Time resolved data acquisition</i>							
Isotope	$^{200}\text{Hg}$	$^{208}\text{Pb}$	$^{232}\text{Th}$	$^{238}\text{U}$	$^{239}\text{Pu}$	$^{240}\text{Pu}$	$^{242}\text{Pu}$
Sweeps	800	800	800	800	800	800	800
Dwell time (ms)	10	10	10	10	30	30	30
Channels per mass	1	1	1	1	1	1	1
Acquisition duration(s)	8	8	8	8	24	24	24

Table S-3. Effect of valence adjustment on the chemical yield of Pu and the decontamination factors of U, Th, Hg and Pb

Redox reagent	Chemical yield*, (%)	Reaction time, min	Decontamination factor **			
			<sup>238</sup> U	<sup>232</sup> Th	Hg	Pb
None	28.1 ± 7.6	0	$1.4 \times 10^2$	$2.7 \times 10^3$	$1.4 \times 10^5$	$3.9 \times 10^3$
200 mg ascorbic acid	98.5 ± 3.0	60	$3.9 \times 10^2$	$2.8 \times 10^4$	$7.6 \times 10^4$	$2.6 \times 10^4$
300 mg Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> -100 mg NaNO <sub>2</sub>	100.0 ± 3.0	40	$1.7 \times 10^3$	$2.6 \times 10^4$	$9.9 \times 10^4$	$3.5 \times 10^4$

\* Results are given as the average of three replicates ± standard deviation.

\*\* Results are given as the average of three replicates, the relative standard deviation was in all instances better than 10%.

Table S-4. Comparison of different experimental conditions for the separation of Pu in Danish soil and the removal of interferences exploiting SI-extraction chromatography

Group	Addition of U, µg	Separation condition #	Chemical yield of Pu measured by <sup>242</sup> Pu (%)*	<sup>239+240</sup> Pu concentration measured (Bq/kg)*	Decontamination factor **			
					<sup>238</sup> U	<sup>232</sup> Th	Hg	Pb
1	0	Washing sequence No. 1, 1.0 mL/min Pu eluting solution No. 1, 1.0 mL/min	86.5 ± 13.6	0.17 ± 0.03	1.5 × 10 <sup>4</sup>	5.5 × 10 <sup>3</sup>	1.6 × 10 <sup>4</sup>	3.2 × 10 <sup>4</sup>
2	12	Washing sequence No. 2, 1.0 mL/min Pu eluting solution No. 2, 1.0 mL/min	97.4 ± 2.9	0.57 ± 0.03	9.4 × 10 <sup>3</sup>	5.4 × 10 <sup>4</sup>	5.1 × 10 <sup>3</sup>	2.3 × 10 <sup>4</sup>
3	0	Washing sequence No. 2, 1.0 mL/min Pu eluting solution No. 2, 1.0 mL/min	89.4 ± 2.7	0.33 ± 0.02	8.8 × 10 <sup>2</sup>	2.4 × 10 <sup>4</sup>	1.2 × 10 <sup>4</sup>	3.2 × 10 <sup>4</sup>
4	10.6	Washing sequence No. 3, 1.0 mL/min Pu eluting solution No. 2, 1.0 mL/min	86.3 ± 2.7	0.52 ± 0.03	9.6 × 10 <sup>2</sup>	3.1 × 10 <sup>4</sup>	8.8 × 10 <sup>3</sup>	4.0 × 10 <sup>4</sup>
5	0	Washing sequence No. 3, 1.0 mL/min Pu eluting solution No. 2, 1.0 mL/min	83.0 ± 2.5	0.20 ± 0.01	4.0 × 10 <sup>2</sup>	4.0 × 10 <sup>4</sup>	4.1 × 10 <sup>3</sup>	2.2 × 10 <sup>4</sup>
6	0	Washing sequence No. 3, 1.0 mL/min Pu eluting solution No. 3, 1.0 mL/min	81.0 ± 2.4	0.23 ± 0.01	4.5 × 10 <sup>3</sup>	1.0 × 10 <sup>4</sup>	5.2 × 10 <sup>3</sup>	4.0 × 10 <sup>4</sup>
7	14.5	Washing sequence No. 3, 1.0 mL/min Pu eluting solution No. 3, 1.0 mL/min	81.1 ± 6.5	0.26 ± 0.09	5.4 × 10 <sup>4</sup>	1.9 × 10 <sup>4</sup>	1.0 × 10 <sup>4</sup>	1.1 × 10 <sup>5</sup>
8	13.7	Washing sequence No. 3, 2.5 mL/min Pu eluting solution No. 3, 1.0 mL/min	100.0 ± 3.0	0.20 ± 0.01	6.3 × 10 <sup>4</sup>	2.8 × 10 <sup>4</sup>	1.2 × 10 <sup>4</sup>	9.6 × 10 <sup>4</sup>
9	0	Washing sequence No. 4, 2.5 mL/min Pu eluting solution No. 3, 1.0 mL/min	91.6 ± 14.5	0.25 ± 0.02	1.4 × 10 <sup>5</sup>	1.4 × 10 <sup>4</sup>	3.7 × 10 <sup>4</sup>	1.6 × 10 <sup>4</sup>
10	0	Washing sequence No. 5, 2.5 mL/min Pu eluting solution No. 3, 1.0 mL/min	100.0 ± 0.1	0.25 ± 0.01	1.5 × 10 <sup>5</sup>	3.9 × 10 <sup>4</sup>	1.1 × 10 <sup>4</sup>	8.2 × 10 <sup>3</sup>
11	0	Washing sequence No. 6, 2.5 mL/min Pu eluting solution No. 3, 1.0 mL/min	97.4 ± 4.5	0.25 ± 0.01	1.1 × 10 <sup>5</sup>	1.5 × 10 <sup>4</sup>	4.6 × 10 <sup>4</sup>	1.9 × 10 <sup>4</sup>
12	10.8	Washing sequence No. 3, 5.0 mL/min Pu eluting solution No. 3, 1.0 mL/min	93.6 ± 3.8	0.25 ± 0.02	2.7 × 10 <sup>4</sup>	7.0 × 10 <sup>3</sup>	1.2 × 10 <sup>4</sup>	1.9 × 10 <sup>5</sup>

The reference value of <sup>239+240</sup>Pu concentration in the Danish soil was reported to be 0.238 ± 0.014 Bq/kg.

\* Experimental results are given as the average of three replicates ± standard deviation. \*\* The relative standard deviations were in all instances better than 10%.

# Washing sequence: No.1: 60 mL of 2 mol/L HNO<sub>3</sub> + 40 mL of 6 mol/L HCl

Washing sequence No.2: 40 mL of 2 mol/L HNO<sub>3</sub> + 10 mL of 9 mol/L HCl + 40 mL of 6 mol/L HCl

Washing sequence No.3: 40 mL of 1 mol/L HNO<sub>3</sub> + 10 mL of 9 mol/L HCl + 40 mL of 6 mol/L HCl

Washing sequence No.4: 60 mL of 1 mol/L HNO<sub>3</sub> + 10 mL of 9 mol/L HCl + 40 mL of 6 mol/L HCl

Washing sequence No.5: 40 mL of 1 mol/L HNO<sub>3</sub> + 60 mL of 6 mol/L HCl + 20 mL of 1 mol/L HNO<sub>3</sub>

Washing sequence No.6: 40 mL of 1 mol/L HNO<sub>3</sub> + 60 mL of 9 mol/L HCl + 20 mL of 1 mol/L HNO<sub>3</sub>

Pu eluting solution No. 1: 20 mL of 0.1 mol/L NH<sub>2</sub>OH·HCl-2 mol/L HCl

Pu eluting solution No. 2: 10 mL of 0.1 mol/L  $\text{NH}_2\text{OH}\cdot\text{HCl}$ -0.1 mol/L  $\text{HNO}_3$   
Pu eluting solution No. 3: 10 mL of 0.1 mol/L  $\text{NH}_2\text{OH}\cdot\text{HCl}$ -2 mol/L  $\text{HCl}$ .

Table S-5. Investigation of the effect of the chemical composition of sample matrix on the measurement efficiency of Pu by ICP-MS

Medium	Signal intensity of 1 ng/L $^{242}\text{Pu}$ (CPS)*	Relative counting efficiency (%)
$^{242}\text{Pu}$ in 0.5 mol/L $\text{HNO}_3$	$400 \pm 8$	100
$^{242}\text{Pu}$ in 2 mol/L $\text{HCl}$	$201 \pm 4$	50
$^{242}\text{Pu}$ in 0.1 mol/L $\text{NH}_2\text{OH}\cdot\text{HCl}$ -0.1 mol/L $\text{HNO}_3$	$322 \pm 6$	80.5
$^{242}\text{Pu}$ in 0.1 mol/L $\text{NH}_2\text{OH}\cdot\text{HCl}$ -2 mol/L $\text{HCl}$	$198 \pm 4$	49.5

\* Results are given as the average of three replicates  $\pm$  1 standard deviation



Table S-6. Investigation of carryover effects in the SI-TEVA extraction chromatography system

Sample name	<sup>242</sup> Pu spiked (mBq)	<sup>239</sup> Pu spiked (mBq)	Effluents	Description #	<sup>242</sup> Pu measured (mBq)	<sup>239</sup> Pu measured (mBq)	Carryover ( <sup>242</sup> Pu, %) <sup>\$</sup>	Carryover ( <sup>239</sup> Pu, %) <sup>\$</sup>
Blank-1	0	0	B1E1	First eluate	< DL*	< DL		
			B1E2	Second eluate	< DL	< DL		
Sample-1	27.92	57.01	S1E1	First eluate	27.4 ± 0.1	52.8 ± 0.3		
			S1E2	Second eluate	0.36 ± 0.04	0.70 ± 0.07	1.29	1.23
			S1E3	Third eluate	0.04 ± 0.01	0.35 ± 0.04	0.14	0.61
Blank-2	0	0	B2E1	First eluate	< DL	< DL	<0.01	<0.06
			B2E2	Second eluate	< DL	< DL	<0.01	<0.06
			B2E3	Third eluate	< DL	< DL	<0.01	<0.06
Blank-3	0	0	B3E1	First eluate	< DL	< DL	<0.01	<0.06
			B3E2	Second eluate	< DL	< DL	<0.01	<0.06
Blank-1'	0	0	B1'E1	First eluate	< DL	< DL		
			B1'E2	Second eluate	< DL	< DL		
			B1'E3	Third eluate	< DL	< DL		
Sample-2	41.14	56.33	S2E1	First eluate	41.1 ± 0.2	57.1 ± 0.3		
			S2E2	Second eluate	0.42 ± 0.04	0.52 ± 0.05	1.02	0.92
			S2E3	Third eluate	0.08 ± 0.02	< DL	0.19	<0.06
			S2E4	Eluate of 10 mL of 0.1 mol/L HF	0.08 ± 0.02	< DL	0.19	<0.06
Blank-2'	0	0	B2'E1	First eluate	< DL	< DL	<0.01	<0.06
			B2'E2	Second eluate	< DL	< DL	<0.01	<0.06
			B2'E3	Third eluate	< DL	< DL	<0.01	<0.06
			B2'E4	Eluate of 10 mL of 0.1 mol/L HF	< DL	< DL	<0.01	<0.06
Blank-3'	0	0	B3'E1	First eluate	< DL	< DL	<0.01	<0.06
			B3'E2	Second eluate	< DL	< DL	<0.01	<0.06

\*DL (detection limit) of Pu isotopes: 1.5 pg/L (or 15 fg in 10 mL eluate, corresponding to 0.035 mBq for <sup>239</sup>Pu and 0.002 mBq for <sup>242</sup>Pu).

<sup>\$</sup> Carryover is calculated as the activity of Pu in a given eluate divided by the spiked Pu in the previous sample.

# If not specified, the elution was effected using 10 mL of 0.1 mol/L NH<sub>2</sub>OH·HCl in 2 mol/L HCl

Table S-7. Evaluation of the analytical performance of a permanent TEVA column in an SI setup (continue of Table 1)

Sample number	Addition of $^{239}\text{Pu}$ (mBq)	Chemical yield $^{242}\text{Pu}$ , %	$^{239}\text{Pu}$ measured,		Decontamination factor		
			(mBq)	(%)	$^{238}\text{U}$	$^{232}\text{Th}$	$^{208}\text{Pb}$
21	5.87	85.0	7.71	106.1	$2.2 \times 10^3$	$7.9 \times 10^2$	$1.6 \times 10^3$
22	21.31	95.9	23.12	101.8	$1.6 \times 10^3$	$7.7 \times 10^2$	$1.4 \times 10^3$
23	5.06	100.0	6.83	105.7	$1.3 \times 10^5$	$5.6 \times 10^3$	$1.1 \times 10^4$
24	0.00	88.7	1.57	112.1	$6.1 \times 10^4$	$4.7 \times 10^3$	$8.2 \times 10^3$
25	21.36	100.0	22.40	98.4	$3.3 \times 10^4$	$2.6 \times 10^3$	$5.4 \times 10^3$
26	5.91	103.0	7.43	101.6	$4.0 \times 10^2$	$1.3 \times 10^3$	$2.6 \times 10^3$
27	0.00	100.0	1.44	102.9	$1.5 \times 10^5$	$4.0 \times 10^3$	$8.2 \times 10^3$
28	22.07	100.2	23.47	100.0	$3.3 \times 10^4$	$2.6 \times 10^3$	$4.5 \times 10^3$
29	5.89	90.7	7.86	107.8	$5.9 \times 10^3$	$1.7 \times 10^3$	$3.3 \times 10^3$
30	0.00	92.2	1.55	110.7	$1.1 \times 10^4$	$1.3 \times 10^3$	$2.5 \times 10^3$
31	22.06	101.1	22.77	97.1	$2.8 \times 10^4$	$2.7 \times 10^3$	$5.5 \times 10^3$
32	4.93	94.0	6.04	95.4	$1.9 \times 10^4$	$2.5 \times 10^3$	$5.2 \times 10^3$
33	0.00	104.0	1.44	102.9	$5.5 \times 10^3$	$1.4 \times 10^3$	$3.0 \times 10^3$
34	20.77	78.1	22.20	100.1	$5.6 \times 10^3$	$9.3 \times 10^2$	$1.9 \times 10^3$
35	5.43	65.4	6.97	102.0	$4.3 \times 10^3$	$9.2 \times 10^2$	$1.8 \times 10^3$
36	0.00	77.8	1.40	100.0	$2.3 \times 10^3$	$5.1 \times 10^2$	$1.1 \times 10^3$
37	21.37	72.7	18.89	83.0	$2.3 \times 10^3$	$6.7 \times 10^2$	$1.2 \times 10^3$
38	5.43	74.0	4.95	72.5	$4.5 \times 10^3$	$1.5 \times 10^3$	$2.2 \times 10^3$
39	0.00	86.1	1.90	135.7	$3.8 \times 10^3$	$1.8 \times 10^3$	$3.4 \times 10^3$
40	29.19	64.2	20.60	67.3	$2.8 \times 10^3$	$2.2 \times 10^2$	$2.9 \times 10^3$

Table S-8. Statistic comparison of the determined concentrations of  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$  and  $^{239+240}\text{Pu}$  with the certified, reference or literature values in Table 7

Sample name	$ t _{\text{exp}}\text{-value}$		
	$^{239}\text{Pu}$	$^{240}\text{Pu}$	$^{239+240}\text{Pu}$
IAEA-375 (soil)	2.34	3.12	0.00
IAEA-135 (sediment)	1.23	0.00	1.53
NIST-4359 (seaweed)	1.24	0.35	0.35
Irish Sea Sediment	3.10	0.64	0.58
Thule soil	-	-	0.58
Danish soil	0.00	0.69	0.46

Note: At 95% confidence interval, the critical t-value ( $t_{\text{crit}}$ ) is 4.30 for n=3

## Paper IV

Qiao, J. X., Hou, X. L., Roos, P., Miró, M. Rapid and simultaneous determination of neptunium and plutonium isotopes in environmental samples by extraction chromatography using sequential injection analysis and ICP-MS. *Journal of Analytical Atomic Spectrometry*. 2010, 25, 1769-1779.

# Rapid and simultaneous determination of neptunium and plutonium isotopes in environmental samples by extraction chromatography using sequential injection analysis and ICP-MS

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This paper reports an automated analytical method for rapid and simultaneous determination of plutonium isotopes ( $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ ) and neptunium ( $^{237}\text{Np}$ ) in environmental samples. An extraction chromatographic column packed with TrisKem TEVA<sup>®</sup> resin was incorporated in a sequential injection (SI) system for the isolation of plutonium and neptunium from matrix elements and interfering nuclides. Valence adjustment is a crucial step to ensure the same chemical behavior of plutonium and neptunium onto the TEVA column and consequently to accomplish their simultaneous separation and detection. Distinct procedures were investigated and compared for the adjustment of oxidation states of plutonium and neptunium to Pu(IV) and Np(IV), respectively. A two-step protocol using sulfite and concentrated nitric acid as redox reagents was proven to be the most effective method. The analytical results for both plutonium and neptunium in three reference materials were in agreement with the recommended or literature values at the 0.05 significance level. The developed method is suitable for the analysis of up to 10 g of soil and 20 g of seaweed samples. The extraction chromatographic separation within the SI system for a single sample takes less than 1.5 h. As compared to batchwise procedures, the developed method significantly improves the analysis efficiency, reduces the labor intensity and expedites the simultaneous determination of plutonium and neptunium as demanded in emergency actions.

## Introduction

Plutonium isotopes, namely  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$  and  $^{241}\text{Pu}$ , are continuously being released into the environment by human nuclear activities. Nuclear weapon testing in the 1950–1980s contributed to global contamination, while recent releases are more modest and mainly connected to reprocessing activities of spent nuclear fuel. Whereas plutonium isotopes have been well studied in the environment,  $^{237}\text{Np}$  has been studied to a much less extent.  $^{237}\text{Np}$  was detected in fallout from nuclear weapon testing and the discharges from nuclear reprocessing plants at Sellafield, UK and La Hague, France. It is also continuously generated from  $^{241}\text{Am}$  ( $\alpha$ ,  $t_{1/2} = 433 \text{ y}$ )<sup>1</sup> decay in the environment.

Except  $^{241}\text{Pu}$  all plutonium isotopes as well as  $^{237}\text{Np}$  decay by alpha particle emission and are regarded as highly radiologically toxic pollutants in the environment due to their long half-lives (*i.e.*,  $^{238}\text{Pu}$ : 87.7 yr,  $^{239}\text{Pu}$ : 24110 yr,  $^{240}\text{Pu}$ : 6561 yr and  $^{237}\text{Np}$ : 2144000 yr) and consequently long-term persistence in the environment.<sup>2,3</sup> Therefore, quantitative determination of plutonium and neptunium in various environmental samples is necessary for environmental risk assessment, radiological emergency preparedness and nuclear waste treatment.

Due to the alpha decay mode of plutonium isotopes and  $^{237}\text{Np}$  and their relative low concentration in environmental samples, a thorough chemical separation of plutonium and neptunium from matrix components of sample and interfering elements and radionuclides has to be completed before measurement. Accurate determination of plutonium isotopes and  $^{237}\text{Np}$  requires the use of appropriate tracers to monitor their chemical yields during chemical separation. Ideally, these tracers should have the same chemical behaviour as the analytes but without occurrence in the sample to be analysed. In the past decades, a number of analytical methods have been developed for the determination of plutonium isotopes in the environment and  $^{236}\text{Pu}$  ( $t_{1/2} = 2.858 \text{ yr}$ ),  $^{242}\text{Pu}$  ( $t_{1/2} = 3.75 \times 10^5 \text{ yr}$ ) or  $^{244}\text{Pu}$  ( $t_{1/2} = 8.08 \times 10^7 \text{ yr}$ ) has been used and performed well as a tracer. However, in the case of  $^{237}\text{Np}$ , no such ideal tracer exists. Traditionally, the  $\gamma$ -emitter  $^{239}\text{Np}$  ( $t_{1/2} = 2.35 \text{ d}$ ) has been employed as a tracer for the determination of  $^{237}\text{Np}$  by a vast number of researchers.<sup>4–8</sup>  $^{239}\text{Np}$  is normally produced by neutron activation reaction of  $^{238}\text{U}$  or through alpha decay of  $^{243}\text{Am}$  in a  $^{243}\text{Am}$ - $^{239}\text{Np}$  generator ( $^{243}\text{Am} \rightarrow ^{239}\text{Np} + ^4\text{He}$ ). However, the short-lived  $^{239}\text{Np}$  requires a short timeframe for the production, delivery and utilization, which makes it inconvenient for a researcher. The comparatively short half-life of  $^{239}\text{Np}$  also imposes restriction on the handling time of samples during analysis. To some extent, plutonium isotopes may be produced during the irradiation of  $^{238}\text{U}$  in the reactor, which should be separated from  $^{239}\text{Np}$ , if  $^{239}\text{Pu}$  is required to be determined in the sample. Besides, the interference in the determination of  $^{239}\text{Pu}$  due to  $^{239}\text{Np}$  decay which generates  $^{239}\text{Pu}$  would also be a major issue. Moreover, the measurement of  $^{239}\text{Np}$  needs to be performed by separate gamma spectrometry.<sup>6</sup>

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$^{235}\text{Np}$  ( $t_{1/2} = 396$  d) is a potential tracer for  $^{237}\text{Np}$  determination, however, it decays mainly through electron capture (99.9974%) with very small fractions by alpha decay (0.0026%) and few suitable  $\gamma$ -rays or X-rays from  $^{235}\text{Np}$  can be measured.<sup>1</sup> In addition, the accurate detection of  $^{235}\text{Np}$  is not feasible using ICP-MS due to isobaric interferences and the short half-life of  $^{235}\text{Np}$  which requires a high level of  $^{235}\text{Np}$  activity in order to be measureable by ICP-MS. The presence of  $^{237}\text{Np}$  impurity in the  $^{235}\text{Np}$  tracer and the need to add sufficient amount of  $^{235}\text{Np}$  to be able to obtain a reliable signal in the noisy low-energy region of beta spectrum of liquid scintillation counting (LSC) set high demands for the analytical procedure.<sup>9</sup> Thus,  $^{235}\text{Np}$  is not a suitable tracer of  $^{237}\text{Np}$ .

$^{236}\text{Np}$  ( $t_{1/2} = 1.54 \times 10^5$  yr) is yet another potential tracer for  $^{237}\text{Np}$  determination. It decays through beta emission (12.5%), electron capture (87.3%) and alpha emission (0.16%). As a result of its long half-life, and therefore low specific radioactivity, and very small alpha emission probability,  $^{236}\text{Np}$  is not an ideal isotopic tracer for the determination of  $^{237}\text{Np}$  by alpha spectrometry. Some researchers have utilised this isotope in environmental samples for  $^{237}\text{Np}$  assays with measurement by mass spectrometry.<sup>10–12</sup> However,  $^{236}\text{Np}$  is not easy to generate and thus it is expensive and still not available in a pure form to most researchers.

The chemical behaviour of  $\text{Np(IV)}$  and  $\text{Pu(IV)}$  are similar in nitric and hydrochloric acid media onto anion exchange or extraction chromatographic resins, which offers a potential opportunity to reach the same chemical yield for both plutonium and neptunium during the radiochemical separation and detection. In this case,  $^{242}\text{Pu}$  (sometimes  $^{236}\text{Pu}$  or  $^{244}\text{Pu}$ ) can be used as a tracer to monitor the chemical yields of  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ , as well as  $^{237}\text{Np}$ . This approach overcomes the difficulties in obtaining an appropriate neptunium tracer and offers a means of simultaneous determination of plutonium isotopes and  $^{237}\text{Np}$  in a single analytical procedure. As a result, a significant decrease is expected in the consumption of resins, chemicals and samples, along with an improved sample throughput.

Due to frequently encountered problems in valence adjustment and maintenance of  $\text{Pu(IV)}$  and  $\text{Np(IV)}$  during chemical separation, few works have been reported to date for the simultaneous determination of plutonium and neptunium in environmental samples using plutonium tracer.<sup>13,14</sup> Among these methods, anion exchange chromatography and extraction chromatography have been used for the separation of plutonium and neptunium from matrix and interfering nuclides. Kim *et al.*<sup>14</sup> reported a simultaneous analytical method for  $^{237}\text{Np}$ ,  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  using  $^{242}\text{Pu}$  as a tracer. The chemical separation was performed with an extraction chromatographic (TEVA) column within a sequential injection system. Their method is rapid and automated, but can only handle small sample sizes (up to 4 g). Chen *et al.*<sup>13</sup> concurrently determined  $^{237}\text{Np}$  and  $^{239} + ^{240}\text{Pu}$  in marine sediment and seawater samples exploiting anion exchange chromatographic separation using  $^{242}\text{Pu}$  as a tracer. Their method can handle large sample sizes, such as 10 g of soil or sediment and 200 litres of seawater, but the procedure is tedious and time consuming (normally 3–4 days for 4–8 samples).

In environmental risk assessment and monitoring, especially in radiological emergencies, a large number of samples are normally required to be analysed in a short timeframe. The traditional methods are not suitable because of long analytical times, and low analytical throughput. This work aims to develop a

rapid and automated analytical method for the simultaneous determination of plutonium isotopes and  $^{237}\text{Np}$ .

In our previous work,<sup>15</sup> TEVA resin was proven to feature appropriate separation efficiency, retention capacity and reusability for determination of plutonium isotopes in environmental samples. In the present work, the usage of in-line TEVA resin and  $^{242}\text{Pu}$  as a tracer is explored for the simultaneous and automatic determination of plutonium and neptunium by using a dedicated sequential injection system and detection by ICP-MS.

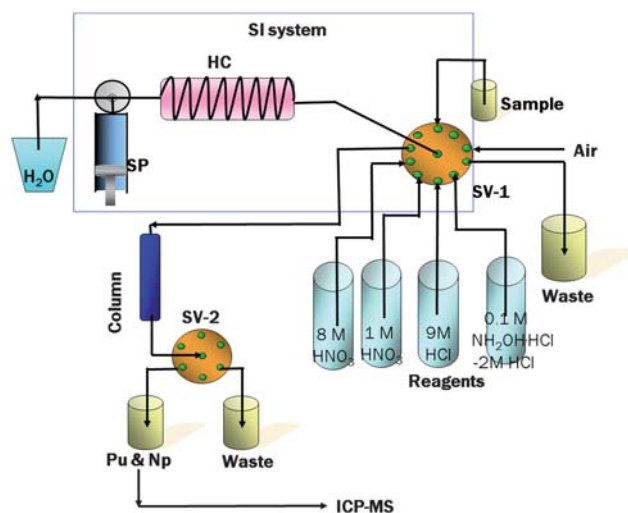
## Experimental

### Instrumentation

An FIALab-3500B Sequential Injection (SI) system (Fig. 1) (FIALab Instruments, Bellevue, WA, USA) consisting of a syringe pump (SP, Cattro, Sunnyvale, CA, USA) with a capacity of 25 mL and an internal 10-port multiple selection valve (SV-1) was computer-controlled via the associated FIALab software. An external 6-port multiple selection valve, *i.e.*, SV-2 (Valco Instruments, Houston, TX, USA), was implemented in the flow network for collection of effluents. The inlet of the separation column was connected to SV-1 and the outlet to the central port of SV-2. All the ports of SV-1 were connected through PEEK ferrules with rigid PTFE tubing (2.4 mm i.d./3.2 mm o.d.) and those of SV-2 through PEEK ferrules with PTFE tubing of smaller internal diameter (0.8 mm i.d./1.6 mm o.d.). The central port of SV-1 was connected to the holding coil (HC), which consisted of PTFE tubing (2.4 mm i.d./3.2 mm o.d.) with an internal volume of 30 mL.

### Standards, reagents and samples

A  $^{242}\text{Pu}$  working solution ( $0.1037 \text{ Bq g}^{-1}$  in  $2 \text{ mol L}^{-1} \text{ HNO}_3$ ) was diluted from NBL-CRM 130 (New Brunswick Laboratory, Argonne, IL, USA). An in-house  $^{239}\text{Pu}$  solution of  $0.100 \text{ Bq g}^{-1}$  in  $2 \text{ mol L}^{-1} \text{ HNO}_3$  was used throughout the experiments. A  $^{237}\text{Np}$  standard solution ( $0.01175 \text{ Bq g}^{-1}$  in  $2 \text{ mol L}^{-1} \text{ HNO}_3$ ) was diluted from NIST-SRM-4341 (National Institute of Standard



**Fig. 1** Schematic diagram of the SI system for simultaneous determination of plutonium and neptunium.

and Technology, Gaithersburg, MD, USA). Standard solutions of uranium and thorium were purchased from NIST (Gaithersburg, MD).

The extraction chromatography resin TEVA (25–50  $\mu\text{m}$ , 50–100  $\mu\text{m}$  or 100–150  $\mu\text{m}$  particle size) was purchased from TrisKem International (Bruz, France). A metered amount of resin was swelled in water and loaded into a PMMA cylindrical column (0.7 cm i.d.  $\times$  10 cm long, 0.7 cm i.d.  $\times$  5 cm long, 0.5 cm i.d.  $\times$  10 cm long or 0.5 cm i.d.  $\times$  5 cm long) and preconditioned with  $\text{HNO}_3$  of identical concentration as the sample medium.

Information concerning the samples analyzed in this work is summarized in Table 1. An artificial cocktail containing 10 mBq of  $^{242}\text{Pu}$ , 1 mBq of  $^{237}\text{Np}$  and 300 mg of  $\text{FeCl}_3$  in 1 mol  $\text{L}^{-1}$   $\text{HNO}_3$  was used to investigate and compare distinct methods for valence adjustment and stabilization of  $\text{Pu(IV)}$  and  $\text{Np(IV)}$ . A Danish mixed soil (NKS inter-comparison sample in Nordic labs for environmental radioactivity) was used throughout for method development.<sup>16</sup> The soil was collected from the top 10 cm at 12 different Danish locations in 2003. The dried soil was ground and sieved through a 0.4 mm sieve. This soil has been analyzed for radionuclides including plutonium isotopes by 3 laboratories during a Nordic round robin inter-comparison, and information values of radionuclides have been published.<sup>16</sup> Because the activity of  $^{237}\text{Np}$  in the Danish soil is three orders of magnitude lower compared to plutonium isotopes (see Table 7 later), the sample (10 g each) was spiked with a given amount of  $^{237}\text{Np}$  (ca. 1 mBq) to increase the signal in ICP-MS detection for the validation of the method.

Three reference materials were analysed in this work for plutonium isotopes and  $^{237}\text{Np}$ , including a sediment (IAEA-135), a seaweed (NIST-SRM-4359) and an Irish Sea sediment. The NIST standard reference material seaweed (a blend of *Fucus vesiculosus*, *Laminaria saccharia* and *Ascophyllum nodosum*) was prepared from seaweed collected from the western coast of Ireland and the White Sea.<sup>17</sup> The Irish Sea sediment was collected from the British coast in the Irish Sea, at a location of 15 km from the Sellafield reprocessing plant, and was freeze dried and sieved through a 0.4 mm sieve.<sup>13</sup>

A Danish seaweed (*Fucus vesiculosus*) and a Thule soil sample were also analysed. The Danish seaweed was collected from the Klint, Danish coast in the Kattegat in July 2003. The sample was first air dried and then oven dried at 70–80  $^\circ\text{C}$  for 2 days,

whereupon the sample was ground and sieved through a 0.4 mm sieve. The Thule soil was collected from 7.5–10 cm top in Thule, Greenland (76 $^\circ$ 27.283N, 69 $^\circ$ 15.355W) in 2003, where a nuclear weapon accident occurred in 1968.

### Sample pre-treatment

For the analysis of soil, sediment and seaweed, sample pre-treatment was conducted before the automatic chemical separation procedure. Fig. 2 shows the overall scheme of sample pre-treatment. A known amount of sample (1–20 g, depending on the concentration level of plutonium and neptunium) was placed in a beaker and ashed at 550  $^\circ\text{C}$  overnight to decompose the organic matter. The sample was spiked with 10 mBq of  $^{242}\text{Pu}$  as a tracer and 0–2 mBq of  $^{237}\text{Np}$  (depending on the sample original composition). The sample was digested in *Aqua regia* on a hot-plate at 150  $^\circ\text{C}$  for 30 min and then at 200  $^\circ\text{C}$  for 2 h to release plutonium and neptunium into solution. During the digestion the beaker was covered with a watch-glass to prevent significant evaporation of the solution, which was occasionally stirred with a glass rod. After cooling, the supernatant was filtered through a GF/A filter to a centrifuge tube and the beaker and filter were washed with 30 mL of 0.2 mol  $\text{L}^{-1}$   $\text{HCl}$ . Concentrated ammonia was added to the supernatant to adjust pH to 8–9 to co-precipitate plutonium and neptunium with  $\text{Fe(OH)}_3$  (for seaweed sample, a certain amount of  $\text{FeCl}_3$  was added into the sample before the co-precipitation) and to remove main matrix constituents such as calcium and magnesium ions. The precipitate was separated by centrifugation and 30 mL of 6 mol  $\text{L}^{-1}$  of  $\text{NaOH}$  was added to the precipitate to remove amphoteric elements, such as aluminium. The final precipitate was then reconstituted as described below and subjected to the extraction chromatographic separation.

### Valence adjustment of plutonium and neptunium to $\text{Pu(IV)}$ and $\text{Np(IV)}$

For the valence adjustment of plutonium and neptunium to  $\text{Pu(IV)}$  and  $\text{Np(IV)}$ , distinct methods were tested and compared. The detailed valence adjustment conditions are discussed under Results and discussion. The final selected valence adjustment method is described as follows.  $\text{HCl}$  was added to the centrifuge

**Table 1** Summary of samples analyzed in this work

Sample	Sample amount	Description	Sampling area/location
Artificial solution	15 mL	10 mBq $^{242}\text{Pu}$ , 1 mBq $^{237}\text{Np}$ and 300 mg of $\text{FeCl}_3$ in 1 mol $\text{L}^{-1}$ $\text{HNO}_3$	Prepared in the lab
Danish soil	10 g	Non-contaminated sample (<1 mBq $\text{g}^{-1}$ of $^{239}\text{Pu}$ )	Top 10 cm of soil from 12 different Danish locations collected in 2003
IAEA-135 sediment	0.5 g	Contaminated sediment	Sediment from Lune Estuary, UK influenced by radioactive discharges from the Sellafield nuclear facility collected in 1991
Irish Sea sediment	1 g	Contaminated sediment	Surface sediment from Irish Sea
NIST-SRM-4359 seaweed	20 g	A blend of <i>Fucus vesiculosus</i> , <i>Laminaria saccharia</i> and <i>Ascophyllum nodosum</i>	Collected from the western coast of Ireland and from the White Sea
Danish Seaweed	20 g	<i>Fucus vesiculosus</i>	Collected from the Klint, Danish coast in the Kattegat
Thule soil	1 g	Contaminated soil	Surface soil from Thule, Greenland

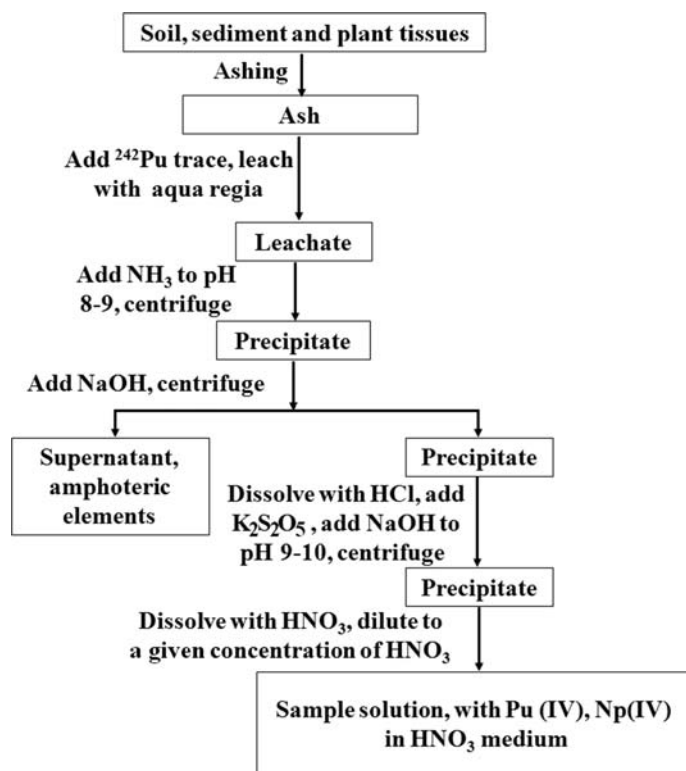


Fig. 2 Sample pre-treatment procedure for simultaneous determination of plutonium and neptunium.

tube to dissolve the precipitate from the pre-treatment step. Afterwards, 200 mg of  $\text{K}_2\text{S}_2\text{O}_5$  (which hydrolyzes into  $\text{KHSO}_3$ ) was added to reduce overall plutonium to  $\text{Pu(III)}$  and neptunium to  $\text{Np(IV)}$ , and the solution was stirred for 10–20 min.  $6 \text{ mol L}^{-1}$  of  $\text{NaOH}$  was then added to the solution to adjust pH to 10 and co-precipitate plutonium and neptunium with  $\text{Fe(OH)}_2$ . The resulting precipitate after centrifugation was dissolved with concentrated  $\text{HNO}_3$  and the solution was finally diluted to  $8 \text{ mol L}^{-1}$   $\text{HNO}_3$  to stabilize  $\text{Pu(IV)}$  and  $\text{Np(IV)}$ .

#### Automated separation scheme

Fig. 3 illustrates the analytical procedure for chemical separation of plutonium and neptunium by means of extraction chromatography using TEVA resin. The procedure carried out using an SI system consists of five steps: (I) Rinsing the holding coil with 50 mL of deionised water and washing sample tubing with  $\text{HNO}_3$  of identical concentration as the sample solution at a flow rate of  $10 \text{ mL min}^{-1}$ ; (II) Aspirating and loading the sample (*ca.* 14 to 28 mL, depending upon the sample size) onto the TEVA column at  $1.0 \text{ mL min}^{-1}$ ; (III) Rinsing the column with  $\text{HNO}_3$  (the volume and concentration of  $\text{HNO}_3$  depending on the rinsing sequence condition, see the detailed information under Results and discussion) to remove uranium and matrix elements, and then 60 mL of  $9 \text{ mol L}^{-1}$   $\text{HCl}$  to remove thorium at  $2.5 \text{ mL min}^{-1}$ ; (IV) Eluting plutonium isotopes and neptunium with 10 mL of  $0.1 \text{ mol L}^{-1}$   $\text{NH}_2\text{OH} \cdot \text{HCl}$ - $2 \text{ mol L}^{-1}$   $\text{HCl}$  at  $1.0 \text{ mL min}^{-1}$ .

After elution of plutonium and neptunium, the eluate was evaporated to dryness on a hot-plate, concentrated nitric acid was added and the solution was again evaporated to dryness to remove  $\text{HCl}$  and  $\text{NH}_2\text{OH} \cdot \text{HCl}$  in the elute. The residue was

reconstituted in 5 mL of  $0.5 \text{ mol L}^{-1}$   $\text{HNO}_3$  and delivered to ICP-MS for detection of  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$  and  $^{237}\text{Np}$ .

#### Determination of plutonium isotopes and neptunium-237 using ICP-MS

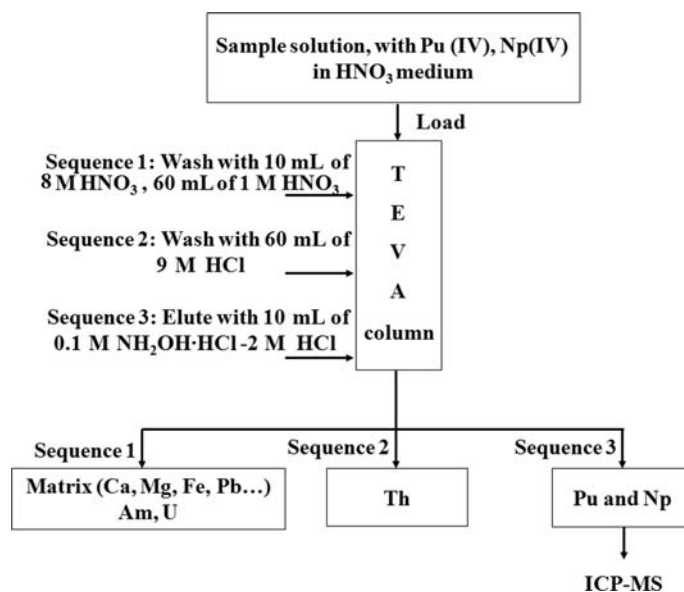
To 5 mL of diluted original or processed sample solution (in  $0.5 \text{ mol L}^{-1}$   $\text{HNO}_3$ ),  $50 \mu\text{L}$  of  $100 \mu\text{g L}^{-1}$   $\text{In(III)}$  (as  $\text{InCl}_3$ ) was added as internal standard. The concentrations of  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{242}\text{Pu}$  and  $^{237}\text{Np}$  were measured by inductively coupled plasma mass spectrometry (ICP-MS; X Series<sup>II</sup> Thermo Fisher Scientific, Waltham, MA) equipped with an Xs-skimmer cone and a concentric nebulizer under hot plasma conditions. The mass resolution and running conditions are given in Table 2. The detection limit calculated as 3SD of processing blank was about  $1.2 \text{ pg L}^{-1}$  for all of  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{242}\text{Pu}$  and  $^{237}\text{Np}$ . A  $0.5 \text{ mol L}^{-1}$   $\text{HNO}_3$  solution was used as washing solution between samples. No carryover effect was observed for consecutive analysis of samples differing up to 3 orders of magnitude in plutonium and neptunium concentrations. The regression analysis of standard solution confirmed a linear correlation over the range of 0.01 to  $100 \text{ ng L}^{-1}$  for plutonium isotopes and  $^{237}\text{Np}$ .

## Results and discussion

### 1. Valence adjustment of plutonium and neptunium to $\text{Pu(IV)}$ and $\text{Np(IV)}$

In the case of using a plutonium isotope as a tracer for the determination of  $^{237}\text{Np}$ , the valence adjustment of plutonium and neptunium to  $\text{Pu(IV)}$  and  $\text{Np(IV)}$  is imperative to ensure the same





**Fig. 3** In-line chemical separation procedure using SI-TEVA extraction chromatography for simultaneous determination of plutonium and neptunium.

behaviour in the chromatographic separation. In this work, we compared distinct methods for valence adjustment and stabilization of Pu(IV) and Np(IV) in terms of chemical yields of plutonium ( $Y_{\text{Pu}}$ ) and neptunium ( $Y_{\text{Np}}$ ) and the ratio of  $Y_{\text{Np}}/Y_{\text{Pu}}$ .

The experimental results compiled in Table 3 and 4 show that, for the artificial solution, the valence adjustment procedure using  $\text{KHSO}_3$ –8 mol  $\text{L}^{-1}$   $\text{HNO}_3$  as redox reagents performed best (see group 1-1 and 2-1 in Table 3). For 10 g of Danish soil, the highest chemical yields for both plutonium ( $88.1 \pm 3.4\%$ ) and neptunium ( $85.7 \pm 3.9\%$ ) were obtained using  $\text{KHSO}_3$ –concentrated  $\text{HNO}_3$  as redox reagents (see group 9 in Table 4). The  $\text{KHSO}_3$ –8 mol  $\text{L}^{-1}$   $\text{HNO}_3$  procedure also performed well to obtain equally high

chemical yields for plutonium and neptunium in soil (see group 8-1 in Table 4). This is in good agreement with earlier results by Chen *et al.*,<sup>13,18</sup> who reported a quantitative conversion of plutonium and neptunium to Pu(III) and Np(IV) with a  $\text{HSO}_3^-$ – $\text{Fe}^{3+}$  redox system in a HCl medium. Concentrated nitric acid was then added to the solution, in which case Pu(III) was oxidized to Pu(IV) by nitrite in the concentrated nitric acid while neptunium remained as Np(IV).

Perna *et al.*<sup>19</sup> suggested a combination of two redox agents, *i.e.*, Mohr's salt (ferrous ammonium sulfate) and  $\text{NaNO}_2$ . The ferrous ammonium sulfate was used to convert simultaneously the overall neptunium species to Np(IV) and plutonium species to Pu(III), then  $\text{NaNO}_2$  was added to oxidize Pu(III) to Pu(IV) while neptunium still was kept at oxidation state IV in 3 mol  $\text{L}^{-1}$   $\text{HNO}_3$  solution. This procedure is rapid and can be completed within 15 min, but it is sensitive to the reaction time. If the reaction time increased to 25 min, Np(V) was generated in the solution. In fact, the investigation of the valence adjustment with the addition of  $\text{NaNO}_2$  to the sample previously treated with  $\text{KHSO}_3$  (see group 8 in Table 3) revealed a large difference between the chemical yields of plutonium and neptunium. This might be due to the generation of Np(V) during the sample loading sequence, which lasted in this work about 30 min for 14 mL of sample solution. Therefore, the above valence adjustment procedure is not suitable for automatic assays employing an SI system, in which a longer waiting time between valence adjustment and sample loading to the column is often required when handling several samples sequentially.

Kim *et al.*<sup>14</sup> examined three redox reagents ( $\text{H}_2\text{O}_2$ ,  $\text{NaNO}_2$  and ascorbic acid) for valence adjustment of plutonium and neptunium in a working solution (3 g  $\text{L}^{-1}$  Fe,  $^{237}\text{Np}$  and  $^{242}\text{Pu}$  tracer in 5 mol  $\text{L}^{-1}$   $\text{HNO}_3$ ), and reported that ascorbic acid was the best reductant on the basis of the recoveries of both elements. With a reaction time of 20 min, around 90% of both elements were recovered, and the longer the reaction time, the better the absolute recoveries. We also investigated the valence adjustment using ascorbic acid in this work (see groups 3, 6 and 7 in Table 4).

**Table 2** Typical operation conditions of ICP-MS for the measurement of plutonium and neptunium

Forward power/W	1400
Gas flow rate/ $\text{L min}^{-1}$	
Coolant	13.8
Auxiliary	0.80
Nebuliser	1.03
<i>Operation pressures/mbar</i>	
Expansion	1.5–2.5
Analysis	$5.3 \times 10^{-8}$
Sample uptake rate/ $\text{mL min}^{-1}$	0.3
Number of replicate runs	3
Typical $^{238}\text{U}/^{238}\text{U}$ ratio	$5 \times 10^{-5}$
Typical plutonium sensitivity (cps per $\text{pg g}^{-1}$ )	200–400
Typical neptunium sensitivity (cps per $\text{pg g}^{-1}$ )	200–400
Typical processing blank at mass 237, 239, 240 and 242 (cps)	1.0–3.0
<i>Time resolved data acquisition</i>	
Isotope	$^{208}\text{Pb}$ $^{232}\text{Th}$ $^{238}\text{U}$ $^{237}\text{Np}$ $^{239}\text{Pu}$ $^{240}\text{Pu}$ $^{242}\text{Pu}$
Sweeps	800 800 800 800 800 800 800
Dwell time/ms	10 10 10 30 30 30 30
Channels per mass	1 1 1 1 1 1 1
Acquisition duration/s	8 8 8 24 24 24 24

**Table 3** Comparison of various valence adjustment conditions and washing sequences for the determination of Pu and Np in artificial solutions<sup>a</sup>

Group	Valence adjustment <sup>b</sup>	Residence time, h <sup>d</sup>	Rinsing sequence <sup>c</sup>	Chemical yield of <sup>242</sup> Pu (Y <sub>Pu</sub> ) (%)	Chemical yield of <sup>237</sup> Np (Y <sub>Np</sub> ) (%)	Ratio of Y <sub>Np</sub> /Y <sub>Pu</sub>
1-1	Condition (1)	0	Condition (1)	81.8 ± 4.1	80.9 ± 4.0	0.99
1-2	Condition (1)	2	Condition (1)	75.5 ± 3.8	80.2 ± 4.0	1.06
1-3	Condition (1)	4	Condition (1)	69.0 ± 3.4	66.7 ± 3.3	0.97
1-4	Condition (1)	6	Condition (1)	51.1 ± 2.6	54.6 ± 2.7	1.07
2-1	Condition (1)	0	Condition (2)	83.3 ± 4.2	81.7 ± 4.1	0.98
2-2	Condition (1)	2	Condition (2)	73.6 ± 3.7	61.0 ± 3.0	0.83
2-3	Condition (1)	4	Condition (2)	42.1 ± 2.1	50.1 ± 2.5	1.19
2-4	Condition (1)	6	Condition (2)	34.2 ± 1.7	34.8 ± 1.7	1.02
3-1	Condition (1)	0	Condition (3)	44.2 ± 2.2	49.7 ± 2.5	1.12
3-2	Condition (1)	2	Condition (3)	30.6 ± 1.5	34.9 ± 1.8	1.14
3-3	Condition (1)	4	Condition (3)	25.1 ± 1.3	28.6 ± 1.4	1.14
3-4	Condition (1)	6	Condition (3)	29.4 ± 1.5	33.5 ± 1.7	1.14
4	Condition (2)	0	Condition (1)	50.5 ± 2.5	55.7 ± 2.8	1.10
5	Condition (2)	0	Condition (2)	58.5 ± 2.9	51.9 ± 2.6	0.89
6-1	Condition (2)	0	Condition (3)	56.9 ± 2.8	63.9 ± 3.2	1.12
6-2	Condition (2)	2	Condition (3)	48.4 ± 2.4	55.2 ± 2.8	1.14
6-3	Condition (2)	4	Condition (3)	54.9 ± 2.8	61.6 ± 3.1	1.12
6-4	Condition (2)	6	Condition (3)	47.4 ± 2.4	54.0 ± 2.7	1.14
7	Condition (2)	0	Condition (4)	100.1 ± 5.0	65.5 ± 3.3	0.65
8	Condition (3)	0	Condition (3)	66.8 ± 3.3	47.7 ± 2.4	0.71

<sup>a</sup> All the values are the average of two replicates (± uncertainty). <sup>b</sup> Valence adjustment: Condition (1): Pu and Np were firstly reduced to Pu(III) and Np(IV) by KHSO<sub>3</sub>, and then the sample solution was prepared by adding 1 mol L<sup>-1</sup> HNO<sub>3</sub>; Condition (2): Pu and Np were firstly reduced to Pu(III) and Np(IV) by KHSO<sub>3</sub>, and Pu(III) was oxidized to Pu(IV) by adding concentrated HNO<sub>3</sub> and then diluted to 8 mol L<sup>-1</sup> HNO<sub>3</sub> solution; Condition (3): Pu and Np were firstly reduced to Pu(III) and Np(IV) by KHSO<sub>3</sub>, and then Pu(III) was oxidized to Pu(IV) by 0.1 mol L<sup>-1</sup> NaNO<sub>2</sub> in 1 mol L<sup>-1</sup> HNO<sub>3</sub> solution. <sup>c</sup> Rinsing sequence: Condition (1): 10 mL of 8 mol L<sup>-1</sup> HNO<sub>3</sub> + 60 mL of 1 mol L<sup>-1</sup> HCl; Condition (2): 60 mL of 4 mol L<sup>-1</sup> HNO<sub>3</sub> + 60 mL of 9 mol L<sup>-1</sup> HCl; Condition (3): 60 mL of 0.1 mol L<sup>-1</sup> NaNO<sub>2</sub>–1 mol L<sup>-1</sup> HNO<sub>3</sub> + 60 mL of 9 mol L<sup>-1</sup> HCl; Condition (4): 60 mL of 8 mol L<sup>-1</sup> HNO<sub>3</sub> + 60 mL of 9 mol L<sup>-1</sup> HCl. <sup>d</sup> Residence time: The time interval between the sample preparation and column separation.

**Table 4** Comparison of various valence adjustment conditions and washing sequences for the determination of plutonium and neptunium in 10 g of Danish soil sample<sup>a</sup>

Group	Valence adjustment <sup>b</sup>	Rinsing sequence <sup>c</sup>	Chemical yield of <sup>242</sup> Pu (Y <sub>Pu</sub> ) (%)	Chemical yield of <sup>237</sup> Np (Y <sub>Np</sub> ) (%)	Ratio of Y <sub>Np</sub> /Y <sub>Pu</sub>	Decontamination factor		
						<sup>238</sup> U	<sup>232</sup> Th	<sup>208</sup> Pb
1	Condition (1)	Condition (1)	3.6 ± 2.8	54.1 ± 7.9	15.03	4.9 × 10 <sup>4</sup>	1.5 × 10 <sup>4</sup>	2.1 × 10 <sup>4</sup>
2	Condition (2)	Condition (1)	5.6 ± 3.8	74.1 ± 7.7	13.23	4.9 × 10 <sup>4</sup>	1.5 × 10 <sup>4</sup>	2.1 × 10 <sup>4</sup>
3	Condition (3)	Condition (1)	0.2 ± 0.1	43.7 ± 8.2	218.50	1.6 × 10 <sup>4</sup>	9.1 × 10 <sup>3</sup>	1.4 × 10 <sup>4</sup>
4	Condition (4)	Condition (1)	76.7 ± 5.6	73.2 ± 6.1	0.95	4.1 × 10 <sup>4</sup>	5.4 × 10 <sup>3</sup>	1.5 × 10 <sup>4</sup>
5	Condition (5)	Condition (1)	53.2 ± 7.5	58.5 ± 9.7	1.10	1.5 × 10 <sup>4</sup>	1.1 × 10 <sup>4</sup>	1.7 × 10 <sup>4</sup>
6	Condition (6)	Condition (1)	2.3 ± 2.8	53.8 ± 7.5	23.39	8.0 × 10 <sup>3</sup>	2.4 × 10 <sup>4</sup>	2.6 × 10 <sup>4</sup>
7	Condition (7)	Condition (1)	84.5 ± 9.8	48.7 ± 8.9	0.58	7.1 × 10 <sup>4</sup>	1.7 × 10 <sup>4</sup>	1.0 × 10 <sup>5</sup>
8-1	Condition (8)	Condition (1)	81.8 ± 4.1	80.9 ± 4.0	0.99	1.5 × 10 <sup>4</sup>	2.0 × 10 <sup>4</sup>	7.8 × 10 <sup>3</sup>
8-2	Condition (8)	Condition (2)	42.1 ± 2.1	50.1 ± 2.5	1.19	2.6 × 10 <sup>4</sup>	2.8 × 10 <sup>4</sup>	6.6 × 10 <sup>3</sup>
9	Condition (9)	Condition (1)	88.1 ± 3.4	85.7 ± 3.9	0.97	1.0 × 10 <sup>4</sup>	7.0 × 10 <sup>3</sup>	1.0 × 10 <sup>4</sup>

<sup>a</sup> All the values are the average of three replicates (± standard deviation). <sup>b</sup> Valence adjustment: Condition (1): Pu and Np were firstly reduced to Pu(III) and Np(IV) by KHSO<sub>3</sub>, and then the sample solution was prepared by adding 1 mol L<sup>-1</sup> HNO<sub>3</sub>; Condition (2): Pu and Np were firstly reduced to Pu(III) and Np(IV) by KHSO<sub>3</sub>, and Pu(III) was oxidized to Pu(IV) by adding concentrated HNO<sub>3</sub> and then dilute to 1 mol L<sup>-1</sup> HNO<sub>3</sub> solution; Condition (3): Pu and Np were firstly reduced to Pu(III) and Np(IV) by KHSO<sub>3</sub>, and Pu(III) was oxidized to Pu(IV) by adding concentrated HNO<sub>3</sub> and dilute to 1 mol L<sup>-1</sup> HNO<sub>3</sub> solution, finally 300 mg of ascorbic acid was added to the sample solution; Condition (4): Pu and Np were firstly reduced to Pu(III) and Np(IV) by KHSO<sub>3</sub>, and Pu(III) was oxidized to Pu(IV) by adding concentrated HNO<sub>3</sub> and then dilute to 4 mol L<sup>-1</sup> HNO<sub>3</sub> solution; Condition (5): Pu and Np were firstly reduced to Pu(III) and Np(IV) by KHSO<sub>3</sub>, and Pu(III) was oxidized to Pu(IV) by adding concentrated HNO<sub>3</sub> and dilute to 4 mol L<sup>-1</sup> HNO<sub>3</sub> solution, finally 300 mg of ascorbic acid was added to the sample solution; Condition (6): Pu and Np were firstly reduced to Pu(III) and Np(IV) by KHSO<sub>3</sub>, and then Pu(III) was oxidized to Pu(IV) by 4 mol L<sup>-1</sup> HNO<sub>3</sub>, finally 300 mg of ascorbic acid was added to the sample solution and stay for 1 h; Condition (7): Pu and Np were firstly reduced to Pu(III) and Np(IV) by KHSO<sub>3</sub>, and then Pu(III) was oxidized to Pu(IV) by 4 mol L<sup>-1</sup> HNO<sub>3</sub>, finally 300 mg of ascorbic acid was added to the sample solution and stir for 1 h; Condition (8): Pu and Np were firstly reduced to Pu(III) and Np(IV) by KHSO<sub>3</sub>, and then Pu(III) was oxidized to Pu(IV) by 8 mol L<sup>-1</sup> HNO<sub>3</sub>; Condition (9): Pu and Np were firstly reduced to Pu(III) and Np(IV) by KHSO<sub>3</sub>, and Pu(III) was oxidized to Pu(IV) by adding concentrated HNO<sub>3</sub> and then dilute to 8 mol L<sup>-1</sup> HNO<sub>3</sub> solution. <sup>c</sup> Rinsing sequence: Condition (1): 10 mL of 8 mol L<sup>-1</sup> HNO<sub>3</sub> + 60 mL of 1 mol L<sup>-1</sup> HNO<sub>3</sub> + 60 mL of 9 mol L<sup>-1</sup> HCl; Condition (2): 60 mL of 4 mol L<sup>-1</sup> HNO<sub>3</sub> + 60 mL of 9 mol L<sup>-1</sup> HCl.

However, when 300 mg of ascorbic acid was directly added into the samples (in 1 mol L<sup>-1</sup> HNO<sub>3</sub>), an extremely low plutonium chemical yield was observed (see group 3 in Table 4), which might be attributed to ascorbic acid preventing the oxidation of Pu(III) to Pu(IV). A similar result was observed when adding 300 mg of ascorbic acid to the sample solution prepared in 4 mol L<sup>-1</sup> HNO<sub>3</sub> after treatment with KHSO<sub>3</sub>, and then keeping the solution for 30 min (see group 6 in Table 4). Although better plutonium chemical yield was obtained when stirring the above mentioned solution for 30 min, the ratio of Y<sub>Np</sub>/Y<sub>Pu</sub> deviated far from 1.0 (see group 7 in Table 4). The failure of the above valence adjustment methods using ascorbic acid might be a consequence of inappropriate redox sequence. When adding ascorbic acid firstly in a diluted acidic sample solution, and then oxidising Pu(III) to Pu(IV) with the addition of concentrated nitric acid (finally diluted to 5 mol L<sup>-1</sup> HNO<sub>3</sub>), equally high chemical yields for plutonium and neptunium could be obtained.<sup>20</sup> In this case, the function of ascorbic acid is the same as KHSO<sub>3</sub> selected in this work, therefore both of these two reagents could be used identically for reducing plutonium and neptunium to Pu(III) and Np(IV).

The investigation of the stability of Pu(IV) and Np(IV) in sample solution reveals that, although the chemical yields of plutonium and neptunium decreased with time from 80% to <50% in 6 h (see groups 1-1 to 1-4 and 2-1 to 2-4 in Table 3), the Y<sub>Np</sub>/Y<sub>Pu</sub> ratios were in all instances close to 1.0, which means <sup>242</sup>Pu is still suitable as a tracer for <sup>237</sup>Np for sample residence times up to 6 h prior to in-line TEVA-based chemical separation.

In order to explain the aforementioned experimental results, it should be borne in mind that HSO<sub>3</sub><sup>-</sup> is able to reduce the high valence states of Np(IV, V, VI), to Np(III) or Np(IV), and Pu(IV, V, VI) to Pu(III) in low acidic media.<sup>18</sup> In the presence of Fe(III), Np(III) would be oxidised to Np(IV) immediately. In fact, the Fe(III)/Fe(II) pair behaves in solution as a redox buffer to preserve Np(IV) from being reduced to Np(III) or oxidised to Np(V, VI). Whenever HNO<sub>3</sub> in a concentration ≥8M is added to the sample after precipitation, Pu(III) is oxidized to Pu(IV) in a few minutes. Np(IV) can be stabilized in a highly concentrated HNO<sub>3</sub> medium, because of the similar *E*<sub>0</sub> between HNO<sub>3</sub>/N<sub>2</sub>O<sub>4</sub> (*E*<sub>0</sub> = +0.79) and Np(V)/Np(IV) (*E*<sub>0</sub> = +0.789), and even though HNO<sub>3</sub> can oxidise Np(IV) to Np(V, VI), the reaction rate would be slow. Yet, if the reaction proceeds longer, Np(IV) might be oxidised to high oxidation states by both nitric acid and the dissolved oxygen in the solution.

## 2. Removal of interferences

Uranium, thorium and lead are naturally abundant elements in most environmental samples. Large amounts of <sup>238</sup>U and isotopes of lead might prevent accurate quantification of <sup>239</sup>Pu, <sup>240</sup>Pu and <sup>237</sup>Np by ICP-MS because of isobaric interferences of polyatomic ions including <sup>238</sup>U<sup>1</sup>H, <sup>238</sup>U<sup>2</sup>H, <sup>202</sup>Hg<sup>37</sup>Cl, <sup>200</sup>Hg<sup>40</sup>Ar, <sup>208</sup>Pb<sup>31</sup>P, <sup>204</sup>Pb<sup>35</sup>Cl, <sup>206</sup>Pb<sup>33</sup>S and tailing of <sup>238</sup>U in 237 and 239 mass regions. In addition, <sup>229</sup>Th and <sup>230</sup>Th would interfere with the potential detection of <sup>242</sup>Pu by alpha spectrometry. Therefore, the removal of these interfering nuclides is important to improve the accuracy of the assays. In this work, decontamination factors for uranium, thorium and lead were calculated using the total amount of a certain nuclide in the sample solution which was loaded onto the column divided by the total amount of that nuclide in the eluate. Table 4 shows that the

decontamination factors for uranium and lead were both higher than 10<sup>4</sup> when using low concentration of nitric acid (1 mol L<sup>-1</sup>) as a washing solution. 10 mL of 8 mol L<sup>-1</sup> HNO<sub>3</sub> was used in the first rinsing step to stabilize Pu(IV) and Np(IV) on the column. According to our earlier findings,<sup>15</sup> a 9 mol L<sup>-1</sup> HCl solution was selected for the removal of thorium, and decontamination factors >10<sup>4</sup> for thorium were achieved.

## 3. Effect of column dimensions

The size and aspect ratio of the TEVA column are important parameters related to the separation efficiency of plutonium and neptunium from matrix interferences, the absolute recoveries and the expenses of chemicals as well. The effect of column dimensions on the above parameters was investigated using the separation procedure described in the experiment section for analysis of 10 g of Danish soil. Experimental results compiled in Table 5 demonstrated that both 1 mL (0.5 cm i.d. × 5 cm long) and 2 mL (0.7 cm i.d. × 5 cm long or 0.5 cm i.d. × 10 cm long) columns met the separation requirements for the real sample, and the measured concentrations of <sup>239</sup> + <sup>240</sup>Pu agreed well with the reference values. However, the recovery of plutonium was extremely low (10.4 ± 1.0%) when using a 4 mL column. This is attributed to the larger void volume of the column (0.7 cm i.d. × 10 cm long) compared with the 1 mL and 2 mL-columns, whereby a 10 mL-eluent volume does not suffice for quantitative elution of plutonium. Accordingly, the elution volume should be increased whenever the SI setup is furnished with separation columns of nominal volumes ≥4 mL.

## 4. Effect of particle size

In general, the larger the specific surface of sorbent beads, the better the separation efficiency. Three particle size ranges of TEVA resin are commercially available, *i.e.*, 25–50 μm, 50–100 μm, 100–150 μm. The analytical performance of the three particle sizes was investigated in the analysis of 10 g Danish soil using a 2 mL-column. The experimental results shown in Table 6 demonstrated that the separation efficiency was not improved by using smaller beads. On the contrary, the decontamination factors for uranium, thorium and lead decreased when increasing the specific surface of TEVA particles. It might be a consequence of the varied flow patterns around the beads and the presence of the boundary layer with slow exchange rate around each particle grain. The reason needs to be further investigated. Considering the build-up of backpressure within the SI network when packing beads less than 100 μm, the TEVA resin with particle size range of 100–150 μm was selected in this work for long-term optimal performance with minimal operational maintenance.

## 5. Method validation and application

To verify the applicability of the analytical method to real-life samples with different matrix composition and complexity, two standard reference materials including IAEA-135 sediment (0.5 g) and NIST seaweed (20 g), and one reference sample (Irish Sea Sediment, 1 g) were analyzed. The analytical results of <sup>237</sup>Np, <sup>239</sup>Pu and <sup>240</sup>Pu for the overall reference materials (see Table 7) do agree well with the recommended or literature-provided values at the 0.05 significance level, even for absolute recoveries ≤60%.

**Table 5** Effect of column aspect ratio on the separation efficiency of Pu in 10 g of Danish soil<sup>a</sup>

Column size	Recovery (%)	<sup>239</sup> + <sup>240</sup> Pu measured, Bq kg <sup>-1c</sup>	Decontamination factor <sup>b</sup>		
			<sup>238</sup> U	<sup>232</sup> Th	<sup>208</sup> Pb
1 mL (0.5 × 5 cm)	85.2 ± 4.2	0.25 ± 0.03	2.9 × 10 <sup>4</sup>	3.4 × 10 <sup>4</sup>	1.0 × 10 <sup>5</sup>
2 mL (0.7 × 5 cm)	75.3 ± 3.8	0.25 ± 0.03	5.8 × 10 <sup>4</sup>	4.3 × 10 <sup>4</sup>	8.2 × 10 <sup>4</sup>
2 mL (0.5 × 10 cm)	86.2 ± 4.3	0.25 ± 0.03	8.2 × 10 <sup>4</sup>	3.1 × 10 <sup>4</sup>	2.2 × 10 <sup>4</sup>
4 mL (0.7 × 10 cm)	10.4 ± 0.5	0.32 ± 0.03	5.9 × 10 <sup>4</sup>	4.7 × 10 <sup>4</sup>	6.0 × 10 <sup>4</sup>

<sup>a</sup> All the values are the average of two replicates (± uncertainty). <sup>b</sup> The relative uncertainties of these values are less than 5%. <sup>c</sup> The reference value of <sup>239</sup> + <sup>240</sup>Pu concentration in the Danish soil is 0.23–0.25 Bq kg<sup>-1</sup>.<sup>16</sup>

This is a consequence of the selection of an appropriate tracer (<sup>242</sup>Pu) for the target radionuclides. The automated protocol rendered improved recoveries when applied to the analysis of Danish seaweed, Danish soil and Thule soil, yet, due to the relatively low levels of <sup>239</sup>Pu, <sup>240</sup>Pu and <sup>237</sup>Np in the Danish seaweed, large standard deviations were found in the experimental results. The analysis of <sup>239</sup> + <sup>240</sup>Pu in Thule soil was also performed using anion exchange chromatography and detection by  $\alpha$ -spectrometry. The average concentration of <sup>239</sup> + <sup>240</sup>Pu was 1.87 ± 0.17 Bq kg<sup>-1</sup>, which does agree well with the analytical results using the SI-TEVA method.

## 6. Analytical performance of SI system

**6.1. Sample throughput.** As described under Experimental, a timeframe of ≥1 day is usually required for handling and analyzing solid samples aimed to determine environmentally-relevant levels of nuclides since sample incineration takes at least 10 h and acid digestion plus precipitation for quantitative recovery of target radionuclides usually take between 3 and 6 h. However, sample incineration and acid digestion can be performed in a batch-wise fashion, and thus up to 20 samples might be processed at a time. Besides, the automated SI-extraction chromatographic separation method is concurrently conducted with pre-treatment of ensuing samples. Considering all the workload involved in the analyses, 16 samples have been proven to be handled within 2 days, which gives rise to a sample throughput of 8 day<sup>-1</sup>. Compared with former batch-wise methods<sup>21,22</sup> handling smaller sample amounts (≤5 g soil *versus* ≤20 g in this work), a better overall sample throughput is still herein achieved.

**6.2. Detection limit and linear range calibration graph.** A pivotal issue to be remarked hereby is that large-sized samples, e.g., 10 g of soil and 20 g of seaweed were processed in this work. The detection limits obtained with the SI-TEVA method for 10 g

of soil, for example, for <sup>239</sup>Pu, <sup>240</sup>Pu and <sup>237</sup>Np were 1.5 mBq kg<sup>-1</sup>, 5.3 mBq kg<sup>-1</sup> and 16 μBq kg<sup>-1</sup>, respectively, and the dynamic linear ranges of the calibration plots for ICP-MS were in the interval of 11.5–1150 mBq kg<sup>-1</sup>, 42.0–4200 mBq kg<sup>-1</sup> and 0.13–13.0 mBq kg<sup>-1</sup>, respectively. Compared with previous publications in which smaller amounts of samples were processed,<sup>21–23</sup> the proposed analytical method yields better enrichment factors and thus improved detection limits and linear ranges of calibration graphs.

**6.3. Remarkable characteristics of SI vs. FI for radionuclide assays.** The different generations of flow analysis, namely, flow injection and sequential injection, have drawn much attention in the automation of extraction chromatographic separations of radionuclides as the entire assay is completely enclosed within the conduits of the manifold. Flow injection analysis however should be deemed ill-suited for radionuclide assays because of the inherent continuous forward-flow pumping of solutions. This entails large consumption of reagents, eluents, and costly isotopes, which are continuously circulating into the conduits of the flow network, and thus wasted when not in use.<sup>23</sup> Besides, FI-setups cannot be exploited in long-term monitoring programs because of the need of periodical recalibration of the peristaltic pump or replacement of the flexible Tygon tubing.

On the contrary, SI systems are fully automated and more versatile than FI manifolds and have the advantage that experimental parameters can be readily changed *via* computer control rather than by physical reconfiguration of the manifold in FI setups. The replacement of the peristaltic pumps by precise digital syringe pumps as liquid drivers fostered the implementation of flow programming protocols which might comprise flow reversals, flow acceleration, and stopped-flow approaches at will, and the handling of well-defined volumes of samples, eluents and acid washing solutions merely at the instant to carry out the correspondent analytical step.<sup>24</sup> For extraction chromatographic

**Table 6** Effect of the particle size of TEVA resin on the separation efficiency of Pu in 10 g of Danish soil<sup>a</sup>

Particle size, μm	Recovery (%)	<sup>239</sup> + <sup>240</sup> Pu measured, Bq kg <sup>-1c</sup>	Decontamination factor <sup>b</sup>		
			<sup>238</sup> U	<sup>232</sup> Th	<sup>208</sup> Pb
25–50	56.0 ± 1.7	0.25 ± 0.02	3.0 × 10 <sup>4</sup>	1.4 × 10 <sup>4</sup>	1.3 × 10 <sup>5</sup>
50–100	61.9 ± 1.9	0.26 ± 0.02	4.6 × 10 <sup>4</sup>	9.8 × 10 <sup>3</sup>	1.6 × 10 <sup>4</sup>
100–150	71.7 ± 2.2	0.25 ± 0.02	5.8 × 10 <sup>4</sup>	4.3 × 10 <sup>4</sup>	5.0 × 10 <sup>4</sup>

<sup>a</sup> All the values are the average of two replicates (± uncertainty). <sup>b</sup> The relative uncertainties of these values are less than 5%. <sup>c</sup> The reference value of <sup>239</sup> + <sup>240</sup>Pu concentration in the Danish soil is 0.23–0.25 Bq kg<sup>-1</sup>.<sup>16</sup>

**Table 7** Analytical results for the determination of plutonium isotopes and  $^{237}\text{Np}$  in reference materials and real samples<sup>a</sup>

Sample name	Addition of $^{239}\text{Pu}$ , mBq	Addition of $^{237}\text{Np}$ , mBq	Recovery (%)	$^{239}\text{Pu}$ measured Bq kg <sup>-1</sup>	$^{240}\text{Pu}$ measured Bq kg <sup>-1</sup>	$^{237}\text{Np}$ measured Bq kg <sup>-1</sup>	Recommended or literature activity concentration, Bq kg <sup>-1</sup>		
							$^{239}\text{Pu}$	$^{240}\text{Pu}$	$^{237}\text{Np}$
IAEA-135 sediment	0	0	59.7 ± 6.9	125.7 ± 5.4	93.6 ± 2.6	0.78 ± 0.04	123.0 ± 3.8 <sup>13</sup> [0.87] <sup>b</sup>	93.8 ± 2.3 <sup>13</sup> [0.13]	0.846 ± 0.045 <sup>13</sup> [2.86]
Irish Sea Sediment	0	0	64.7 ± 15.9	223.7 ± 7.3	191.3 ± 5.9	1.02 ± 0.04	237.0 ± 5.0 <sup>13</sup> [3.16]	181.0 ± 4.9 <sup>13</sup> [3.02]	0.987 ± 0.048 <sup>13</sup> [1.43]
NIST-4359 Seaweed	0	0	56.4 ± 2.0	0.079 ± 0.003	0.052 ± 0.005	0.000134 ± 0.000020	0.084 ± 0.003 <sup>17</sup> [1.73]	0.057 (0.049–0.066) <sup>17</sup> [1.73]	0.000173 (0.000152–0.000198) <sup>17 c</sup> [3.38]
Danish soil	0	0.50 ± 0.03	88.1 ± 3.4	0.14 ± 0.01	0.09 ± 0.02	0.05 ± 0.01	0.140 ± 0.008 <sup>16</sup> [0.69]	0.098 ± 0.006 <sup>16</sup> [0.69]	(5.08 ± 0.158) × 10 <sup>-4</sup> 16
Thule soil	0	1.02 ± 0.12	70.0 ± 9.5	1.45 ± 0.07	0.37 ± 0.07	1.14 ± 0.16	—	—	—
Danish seaweed	8.13 ± 0.10	1.67 ± 0.03	77.8 ± 11.4	0.40 ± 0.02	0.01 ± 0.01	0.08 ± 0.01	—	—	—
Danish seaweed	0	0	79.3 ± 10.5	0.02 ± 0.01	0.02 ± 0.01	<DL	—	—	—

<sup>a</sup> All values are the average of three replicates (± standard deviation). <sup>b</sup> Numbers in brackets are  $t_{\text{exp}}$ -values, at the 95% confidence interval, the critical  $t$ -value ( $t_{\text{crit}}$ ) is 4.30 for  $n = 3$ . <sup>c</sup> The information value of  $^{237}\text{Np}$  in the certification paper of NIST-4359 seaweed was provided by our laboratory in Risø-DTU; however, the unit for  $^{237}\text{Np}$  activity on the certification datasheet was incorrectly presented. The correct value should be 0.17 mBq kg<sup>-1</sup> with a range of 0.152–0.198 mBq kg<sup>-1</sup>.

separations, samples, eluents, washing solutions and standards can be all nested around a multi-position selection valve in SI, which replaces rotary injection valves in FI, and sequentially selected for delivery to the column, with minimum analyst intervention.<sup>2,25–27</sup> The instrumental simplicity, flexibility, robustness, and ease with which hydrodynamic variables can be controlled in SI, have turned it into a very appealing analytical technique for automation of radionuclide assays.

## Conclusions and perspective

The SI-extraction chromatographic method herein proposed for concurrent determination of plutonium and neptunium in environmental samples is automatic, rapid and minimizes the expense of sorbent and chemicals.  $^{242}\text{Pu}$  performed well as a tracer for both plutonium isotopes and neptunium, thereby overcoming the limitations in getting an appropriate neptunium tracer for  $^{237}\text{Np}$ . The developed method is versatile as it can be applied to the analysis of different kinds of environmental matrices, such as soil, sediment and seaweed.

However, the recoveries of plutonium isotopes and neptunium are in some instances ≤60% in case of using TEVA as a chromatographic separation resin. This might be attributed to the low affinity of plutonium and neptunium onto the TEVA resin in highly concentrated nitric acid medium. Beside, the short-time stability of Np(IV) would be another limitation for use of the sequential injection system in the consecutive separation of a large number of samples. Therefore, potential parameters that actually should be investigated are to cool the sample solution down to allow for longer residence times of Np(IV) and to heat the column using a temperature regulating mantle during the separation to increase the exchange rate on the resin and therefore shorten the separation time.

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## Paper V

Qiao, J. X., Hou, X. L., Roos, P., Miró, M. Reliable determination of  $^{237}\text{Np}$  using  $^{242}\text{Pu}$  as a potential tracer. *Talanta*. 2011, 84, 494-500.





# Reliable determination of $^{237}\text{Np}$ in environmental solid samples using $^{242}\text{Pu}$ as a potential tracer

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## ABSTRACT

This paper reports an analytical method for rapid determination of neptunium ( $^{237}\text{Np}$ ) in environmental solid samples exploiting automated sequential injection (SI)-based anion exchange separation. Pivotal issues on analytical method performance were investigated including sorption behavior of  $^{237}\text{Np}$  onto various AG 1-type anion exchangers; suitability of  $^{242}\text{Pu}$  as a tracer for  $^{237}\text{Np}$  determination in environmental solid samples; and long-term chemical stability of tetravalent Np. Experimental results revealed that the degree of resin cross-linking has a significant influence on the separation efficiency in terms of chemical yields of  $^{237}\text{Np}$  and removal of interfering nuclides. Although ca. 30% of sorbed Np onto AG 1- $\times$ 4 was stripped out during HCl rinsing step for the removal of Th, chemical yield ratios of  $^{237}\text{Np}$  to  $^{242}\text{Pu}$  were proven steady with an average value of  $0.67 \pm 0.04$  ( $n = 15$ ) under selected experimental conditions. Disulfite-8 M  $\text{HNO}_3$  was selected as a redox pair for valence adjustment to Np(IV) and the tetravalent Np in the sample solution was demonstrated to be stabilized for up to 5 days under  $3^\circ\text{C}$ . The analytical results for reference materials showed a good agreement with the expected values, thereby demonstrating the usefulness of  $^{242}\text{Pu}$  as a non-isotopic tracer for  $^{237}\text{Np}$  chemical yield monitoring. The on-column separation procedure fosters rapid analysis as required in emergency situations since each individual sample can be handled within 2.5 h, and leads to a significant decrease in labor intensity compared to conventional batch-wise protocols.

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## 1. Introduction

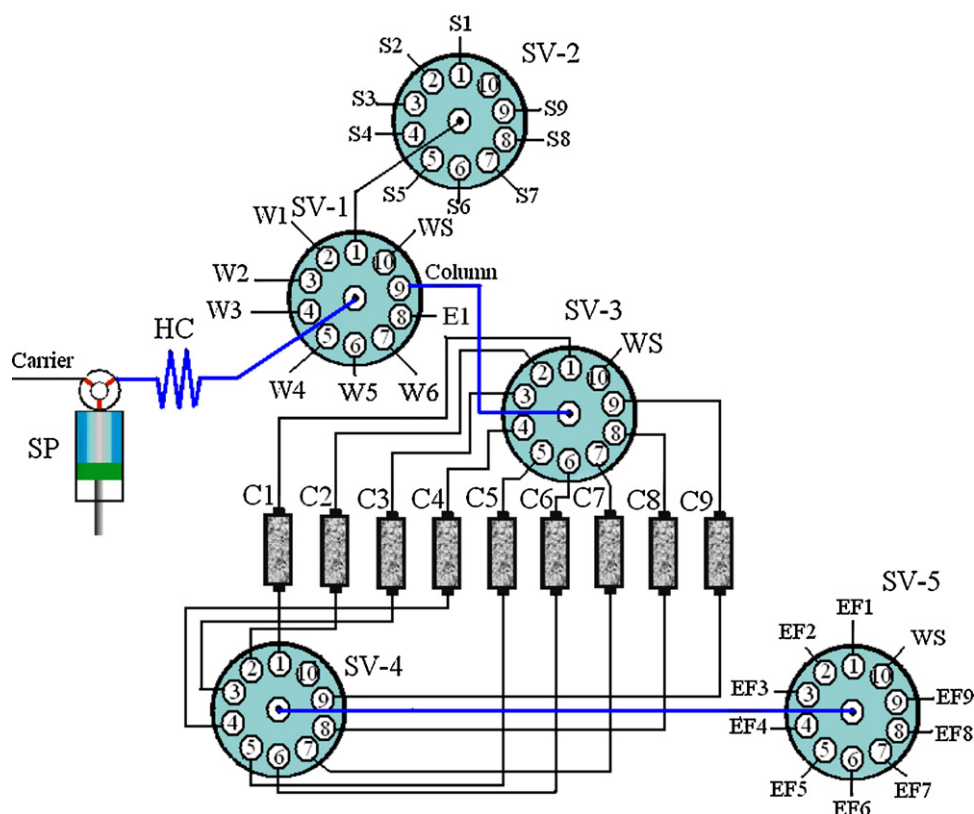
Neptunium is the first transuranium element (TRU) with  $^{237}\text{Np}$  as the most important long-lived isotope, which is an alpha emitter with half-life of  $(2.144 \pm 0.007) \times 10^5$  years. The main sources of  $^{237}\text{Np}$  in the environment are nuclear weapon tests, controlled releases from nuclear reprocessing plants, especially at La Hague (France) and Sellafield (UK), and nuclear accidents, e.g., Chernobyl in 1986 [1]. Due to the considerably longer half-life compared with other actinides, for example  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ , the activity of  $^{237}\text{Np}$  is relatively low. However, it will be the prevailing TRU element in nuclear waste after a few hundred years, where most of plutonium and uranium are removed while neptunium together with other transuranics and fission and activation products go to the high active waste fraction for final disposal [1]. Besides, neptunium is one of the most hazardous radionuclides in spent nuclear fuel due to the relatively high mobility especially under oxic conditions. Therefore, accurate determination of  $^{237}\text{Np}$  in environmental samples is important for radioecological studies, environmen-

tal risk assessment, emergency preparedness and nuclear waste treatment.

A number of analytical methods including co-precipitation, solvent extraction, ion exchange chromatography and extraction chromatography have been reported for the determination of  $^{237}\text{Np}$  in environmental samples [2–15] and the analytical features thereof have been critically ascertained in recent review articles [16,17]. The major obstacle in accurate  $^{237}\text{Np}$  determination lies in the need to obtain a reliable chemical yield isotopic tracer. In fact, no such ideal tracer is available as of yet because the short-lived  $^{239}\text{Np}$  ( $t_{1/2} = 2.3565 \pm 0.0004$  d) imposes stringent demands on its production and sample handling times during analysis [18]; the long-lived  $^{236}\text{Np}$  ( $t_{1/2} = (1.54 \pm 0.06) \times 10^5$  years) is not easy to generate and still not available commercially in a suitable purity; the applicability of  $^{235}\text{Np}$  ( $t_{1/2} = 396.1 \pm 1.2$  d) is hampered by frequent  $^{237}\text{Np}$  impurities and the need of sufficient amount of  $^{235}\text{Np}$  to obtain a reliable signal with liquid scintillation counting (LSC) [19]. In theory,  $^{237}\text{Np}$  as an alpha emitter could be measured by alpha spectrometry. In practice, however, this is not a straightforward task due to the ultra-trace level of  $^{237}\text{Np}$  in non-contaminated environmental samples plus the low specific activity of the isotope. Accordingly, long measurement times, from 24 h to weeks, are required. Besides, spectrometric interferences from  $^{226}\text{Ra}$ ,  $^{229}\text{Th}$ ,

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**Fig. 1.** Schematic diagram of the sequential injection (SI) system for automated separation of ultra-trace levels of  $^{237}\text{Np}$  in environmental solid samples. S1–S9: samples; W1: 8 M  $\text{HNO}_3$ ; W2: 6 M  $\text{HNO}_3$ ; W3: 4 M  $\text{HNO}_3$ ; W4: 2 M  $\text{HNO}_3$ ; W5: 1 M  $\text{HNO}_3$ ; W6: 9 M  $\text{HCl}$ ; E1: 0.5 M  $\text{HCl}$ ; C1–C9: anion exchange columns; EF1–EF9: eluate fractions; SV1–SV5: multi-position selection valves.

$^{230}\text{Th}$ ,  $^{233}\text{U}$ ,  $^{234}\text{U}$ , and  $^{242}\text{Pu}$  set high demands on the chemical separation when measuring  $^{237}\text{Np}$  by alpha spectrometry.

To overcome the abovementioned problems, a potential avenue would be to exploit a non-isotopic tracer (e.g.,  $^{242}\text{Pu}$ ) to monitor the chemical yield of  $^{237}\text{Np}$  in radiochemical analysis combined with ICP-MS for the detection of  $^{237}\text{Np}$ , since ICP-MS offers advantages of fast measurement and low detection limits over alpha spectrometry [20]. However, articles associated with the application of non-isotopic tracers for  $^{237}\text{Np}$  are scarce. To the best of our knowledge, the reported separation methods are up to date limited to the publications of Chen et al. [7] and Kim et al. [21] using anion exchange and extraction chromatography, respectively. Kim et al. [21] reported a flow injection system coupled to ICP-MS for expedient separation of Np and Pu, yet only applicable to the analysis of small sized samples ( $\leq 4\text{ g}$  of soil). In our former work [22], we succeeded in Np determination using a non-isotopic Pu tracer via extraction chromatography (TEVA), however, as compared with anion exchange chromatography, extraction chromatography is more costly and less feasible for widespread use in radiochemical laboratories for routine assays. Notwithstanding the fact that quantitative isolation of Np was reported by Chen et al. [7] using anion exchange chromatography, the chemical separation protocol was labor-intensive and time-consuming since several separation techniques were combined in a batch-wise fashion including precipitation, solvent extraction and anion exchange chromatography.

In this work, we aim to investigate the suitability and actual applicability of  $^{242}\text{Pu}$  as a non-isotopic tracer for rapid determination of  $^{237}\text{Np}$  using SI-anion exchange separation and ICP-MS detection. Sorption performances of  $^{237}\text{Np}$  and  $^{242}\text{Pu}$  onto anion exchangers are investigated in detail for a variety of column dimensions and sorbent materials. To the best of our knowledge, no automatic flow-based method using gel-type anion exchanger has

been reported to date for the determination of  $^{237}\text{Np}$  at environmentally relevant levels.

## 2. Experimental

### 2.1. Experimental setup

A schematic illustration of the automated separation set-up is shown in Fig. 1. It consists of an FIALab-3500B SI system (FIALab Instruments, Bellevue, WA, USA) furnished with a syringe Pump (SP, Cavo, Sunnyvale, CA, USA, 25 ml capacity), an internal 10-port multi-position selection valve (SV-1), four external 10-port multi-position section valves, SV-2 to SV-5 (Valco Instruments, Houston, TX, USA), and nine separation columns. Operation of the system was computer controlled via FIALab software. All outlets of the selection valve (SV-1) were connected through PEEK ferrules with rigid PTFE tubing (2.4 mm i.d./3.2 mm o.d.) and all outlets of the external selection valves (SV-2 to SV-5) were connected through PEEK ferrules with rigid PTFE tubing of smaller diameter (0.8 mm i.d./1.6 mm o.d.). The central port of the SV-1 was connected to the holding coil (HC), which consists of a 6.6 m-long PTFE tubing with an inner capacity of 30 ml (2.4 mm i.d./3.2 mm o.d.). In order to improve the sample throughput, nine columns were implemented in the SI system at a time and thus nine samples were able to be processed consecutively in a fully automated fashion. Each column was proven to be reused up to three times.

### 2.2. Standards, reagents and samples

All reagents, including nitric acid ( $\text{HNO}_3$ ), hydrochloride acid ( $\text{HCl}$ ), ammonia ( $\text{NH}_3\cdot\text{H}_2\text{O}$ ), potassium disulfite ( $\text{K}_2\text{S}_2\text{O}_5$ ) and sodium hydroxide ( $\text{NaOH}$ ) used in the experiment were of ana-

lytical reagent grade.  $^{242}\text{Pu}$  standard solution ( $0.1037\text{ Bq g}^{-1}$  in  $2\text{ M HNO}_3$ ) was diluted from NBL-CRM 130 purchased from New Brunswick Laboratory (Argonne, IL, USA).  $^{237}\text{Np}$  solution of  $0.01175\text{ Bq g}^{-1}$  in  $2\text{ M HNO}_3$  was diluted from a stock solution supplied by Risø National Laboratory for Sustainable Energy (Denmark). Standard solutions of uranium and thorium were purchased from NIST (Gaithersburg, MD, USA).  $^{239}\text{Np}$  was separated from a  $^{243}\text{Am}$  stock solution as follows: the  $^{243}\text{Am}$  solution was first loaded onto an anion exchange column, after washing with  $9\text{ M HCl}$  to remove all  $^{243}\text{Am}$ ,  $^{239}\text{Np}$  (the daughter of  $^{243}\text{Am}$ ) was eluted with  $2\text{ M HCl}$ . All solutions used in the experiments were prepared with deionised water ( $18\text{ M}\Omega\text{ cm}$ , purified using a water purification system from Sartorius Stedim Biotech, Aubagne Cedex, France).

AG 1-type anion exchangers are the resins of choice for Np separation in most of radioanalytical laboratories [2,3,6,7,15,23,24]. In this work, AG 1-type resins with different cross-linkages and particle sizes were explored including AG 1- $\times$ 2 (2% cross-linkage, 50–100 mesh), AG 1- $\times$ 4 (4% cross-linkage, either 50–100 mesh or 100–200 mesh) and AG 1- $\times$ 8 (8% cross-linkage, 50–100 mesh) in chloride form (Bio Rad Laboratories Inc., Hercules, CA, USA). Resin beads were swelled in water and poured into a cylindrical Econo-Column® (Bio-Rad Laboratories Inc.), followed by pre-conditioning with  $25\text{ ml}$  of  $8\text{ M HNO}_3$  prior to use. The effect of column size and aspect ratio on the separation of  $^{237}\text{Np}$  was investigated exploiting columns with the following dimensions:  $\varnothing 1.0 \times 20\text{ cm}$  (ca.  $16\text{ ml}$ ),  $\varnothing 0.7 \times 20\text{ cm}$  (ca.  $8\text{ ml}$ ),  $\varnothing 0.7 \times 10\text{ cm}$  (ca.  $4\text{ ml}$ ),  $\varnothing 0.5 \times 10\text{ cm}$  ( $2\text{ ml}$ ),  $\varnothing 0.7 \times 5\text{ cm}$  (ca.  $2\text{ ml}$ ) and  $\varnothing 0.5 \times 5\text{ cm}$  (ca.  $1\text{ ml}$ ).

Method development and investigation of key parameters were performed using  $10\text{ g}$  of a laboratory round-robin inter-comparison material, namely, Danish soil, (unless otherwise stated) spiked with  $^{237}\text{Np}$ . One certified reference material (IAEA-135 sediment) and one reference sample from an inter-comparison exercise (Irish Sea sediment) were utilized as well for evaluation of method trueness. A Danish seaweed (*Fucus vesiculosus*) collected from the Klint, Danish coast was also analysed. The seaweed was first air-dried and then oven-dried at  $70\text{--}80^\circ\text{C}$  for 2 days, whereupon the sample was ground and sieved through a  $0.4\text{ mm}$  sieve.

### 2.3. Sample pre-treatment

$10\text{ g}$  of Danish soil (or  $1.0\text{ g}$  of IAEA-135 sediment/Irish Sea sediment or  $20\text{ g}$  of Danish seaweed) was placed in a beaker and ashed at  $550^\circ\text{C}$  overnight to decompose organic matter. The treated sample was spiked with  $5.0\text{ mBq}$  of  $^{242}\text{Pu}$  as a chemical yield tracer and, in the cases of Danish soil and seaweed, with  $0.50\text{ mBq}$  of  $^{237}\text{Np}$  as well. A detailed explanation of the preliminary sample pre-treatment protocol can be found in our previous publication [22]. In brief, after aqua regia digestion, Np and Pu were co-precipitated with iron oxyhydroxides and thus isolated from the major components of the sample matrix.

### 2.4. Valence adjustment to Pu(IV) and Np(IV)

The redox pair  $\text{K}_2\text{S}_2\text{O}_5\text{--}8\text{ M HNO}_3$  was utilized for valence adjustment of the target radionuclide and tracer to Np(IV) and Pu(IV), respectively. The complete analytical sequence has been described elsewhere [22].

### 2.5. Automated separation scheme

The SI-anion exchange chromatographic procedure consists of four steps as follows: (I) rinsing the holding coil with  $50\text{ ml}$  of deionised water, and overall manifold tubing with in total  $50\text{ ml}$  of  $8\text{ M HNO}_3$  at a flow rate of  $10\text{ ml min}^{-1}$ ; (II) loading the sample ( $14\text{ ml}$  per assay) onto the anion exchange column at  $1.0\text{ ml min}^{-1}$ ;

(III) rinsing the column with  $100$  or  $200\text{ ml}$  ( $100\text{ ml}$  for  $2\text{ ml}$ -column and  $200\text{ ml}$  for  $4, 8, 16\text{ ml}$ -column, respectively) of  $8\text{ M HNO}_3$  at  $2.5\text{ ml min}^{-1}$  to remove most of the matrix elements and uranium, followed by  $100\text{ ml}$  of  $9\text{ M HCl}$  to remove thorium; (IV) eluting Np and Pu with  $40$  or  $100\text{ ml}$  of  $0.5\text{ M HCl}$  ( $40\text{ ml}$  for  $2, 4, 8\text{ ml}$ -column and  $100\text{ ml}$  for  $16\text{ ml}$ -column, respectively) at  $2.5\text{ ml min}^{-1}$ .

The eluate was evaporated to dryness on a hot-plate to eliminate hydrochloric acid. The residue was dissolved in  $5\text{ ml}$  of  $0.5\text{ M HNO}_3$  and the resultant solution was analysed by ICP-MS for quantification of  $^{237}\text{Np}$ ,  $^{242}\text{Pu}$  and interfering nuclides.

### 2.6. ICP-MS detection of $^{237}\text{Np}$ and $^{242}\text{Pu}$

To  $5\text{ ml}$  of processed sample (diluted in  $0.5\text{ M HNO}_3$ ),  $50\text{ }\mu\text{l}$  of  $100\text{ }\mu\text{g l}^{-1}$  In(III) (as  $\text{InCl}_3$ ) were added as an internal standard to correct the potential transmission variations in ICP-MS instrument. The concentrations of  $^{237}\text{Np}$ ,  $^{242}\text{Pu}$ ,  $^{238}\text{U}$  and  $^{232}\text{Th}$  were determined by X Series<sup>II</sup> inductively coupled plasma-mass spectrometry (ICP-MS) (Thermo Fisher Scientific, Waltham, MA, USA) equipped with an Xs-skimmer core and a concentric nebulizer under hot plasma conditions. The typical operational conditions for ICP-MS detection of the above radionuclides are given elsewhere [22].

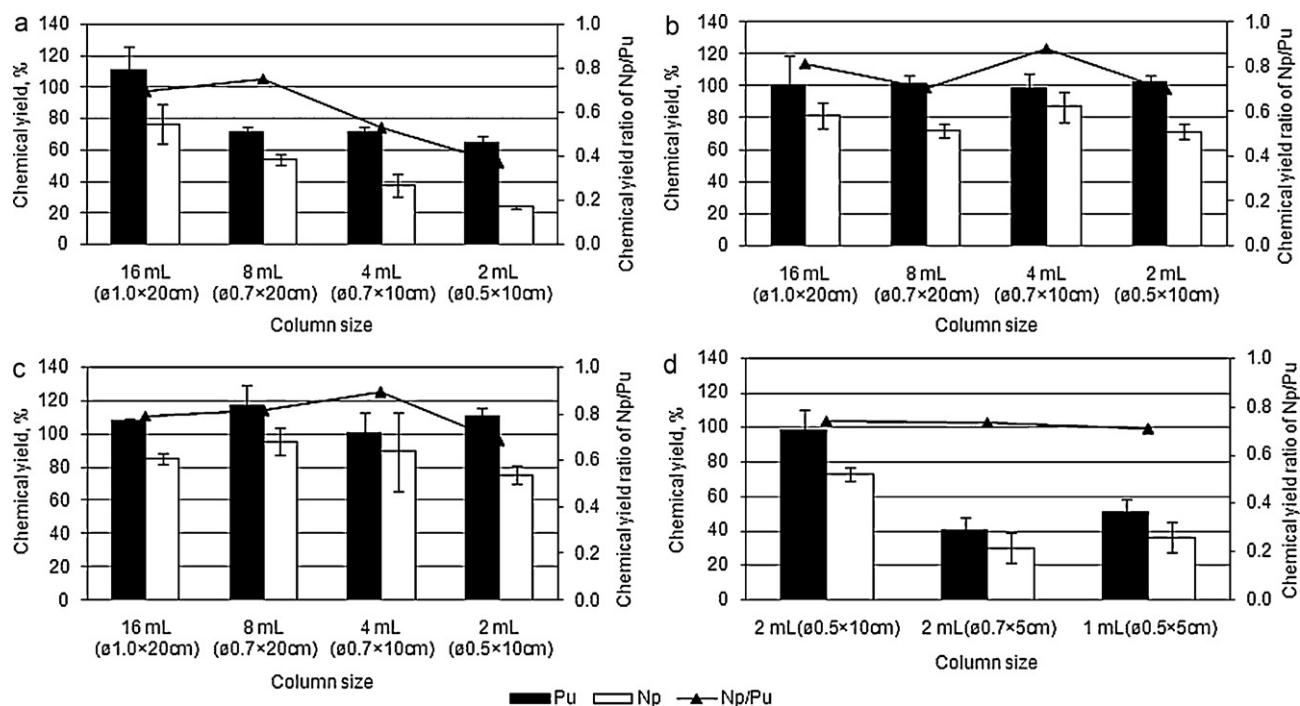
## 3. Results and discussion

In brief, this work aimed at setting an automated SI-based chromatographic procedure where both Pu and Np are sorbed strongly and equally well in the separation platform. To facilitate measurement using a sensitive detection method (ICP-MS) the protocol should be able to remove matrix elements which might cause serious spectral and non-spectral interfering effects. This mainly holds true to uranium but thorium needs to be kept to minimum levels as well.

### 3.1. Selection of separation protocol and column dimensions

The main challenge whenever using  $^{242}\text{Pu}$  as a non-isotopic tracer for  $^{237}\text{Np}$  determination is to obtain similar uptake and elution behavior for Pu and Np during the separation process and to ensure closely equal chemical yields. Column dimensions and physicochemical properties of anion exchangers including cross-linkage and particle size were investigated as core parameters for expedient uptake of both radionuclides. Fig. 2 shows the chemical yields of Np and Pu in connection with columns of varied dimensions packed with diverse anion exchangers, namely, AG 1- $\times$ 2 (50–100 mesh), AG 1- $\times$ 4 (50–100 mesh), AG 1- $\times$ 8 (50–100 mesh) and AG 1- $\times$ 4 (100–200 mesh). Because of the need of quantitative removal of uranium to reduce the interference of tailing of  $^{238}\text{U}$  at  $m/z = 237$  in ICP-MS, the decontamination factor for uranium, i.e. the ratio of total amount of uranium in the sample loading solution and that in the eluate, was also compared among distinct resins (see Fig. 3).

Experimental results revealed the existence of significant differences between the chemical yields of  $^{237}\text{Np}$  and  $^{242}\text{Pu}$  regardless of column dimensions and cross-linkage. The chemical yields ratio  $^{237}\text{Np}$  to  $^{242}\text{Pu}$  in AG 1- $\times$ 2 decreased dramatically when reducing the column size. On the other hand, chemical yield ratios of  $^{237}\text{Np}/^{242}\text{Pu}$  in AG 1- $\times$ 4 and AG 1- $\times$ 8 were unrelated to column size, with steady values at ca.  $0.7$ , even employing small-sized ( $2\text{ ml}$ ) columns for separation. However, AG 1- $\times$ 4 resin was superior to AG 1- $\times$ 8 regarding decontamination of uranium with factors within the range of  $10^3\text{--}10^4$  for AG 1- $\times$ 4 vs.  $10^2\text{--}10^3$  for AG 1- $\times$ 8 when using  $2\text{ mL}$  ( $\varnothing 0.5 \times 10\text{ cm}$ ) of columns. The small sized AG 1- $\times$ 4 column ( $\varnothing 0.5 \times 10\text{ cm}$ ) was regarded as the most suitable choice because of elevated Pu chemical yields ( $>95\%$ ) and fairly high



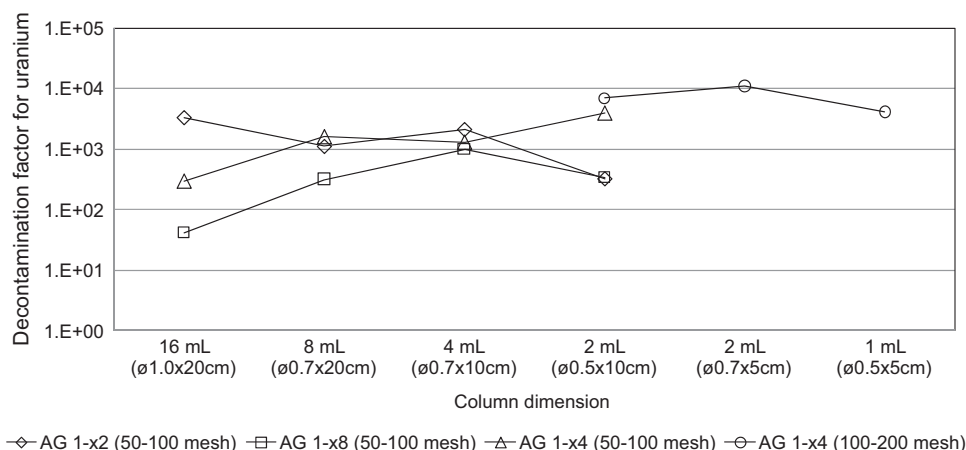
**Fig. 2.** Chemical yields of Np and Pu using distinct strong basic anion exchangers including (a) AG 1- $\times$ 2 (50–100 mesh), (b) AG 1- $\times$ 4 (50–100 mesh), (c) AG 1- $\times$ 8 (50–100 mesh) and (d) AG 1- $\times$ 4 (100–200 mesh) with columns of different capacity including 1 mL ( $\varnothing 0.5 \times 5$  cm), 2 mL ( $\varnothing 0.7 \times 5$  cm or  $\varnothing 0.5 \times 10$  cm), 4 mL ( $\varnothing 0.7 \times 10$  cm), 8 mL ( $\varnothing 0.7 \times 20$  cm) and 16 mL ( $\varnothing 1.0 \times 20$  cm) (sample: 10 g of Danish soil; flow rate: 1.0 mL min<sup>-1</sup> for sample loading and 2.5 mL min<sup>-1</sup> for column rinsing and elution).

ratios of  $^{237}\text{Np}/^{242}\text{Pu}$  chemical yields and decontamination factors for uranium, with minimal pressure drop in the flow system, and consequently was selected for further investigation.

The influence of particle surface area and column aspect ratio on the performance of 4% cross-linkage resins is presented in Fig. 2b and d. Although improved decontamination factors for uranium (see Fig. 3) and slightly higher ratios of  $^{237}\text{Np}/^{242}\text{Pu}$  chemical yields were obtained whenever smaller beads were used, undue back pressure was observed which hindered the application of high flow rates in the low-pressure SI network. The column aspect ratio affected the separation efficiency as well: the larger the aspect ratio, the better were the chemical yields of both  $^{242}\text{Pu}$  and  $^{237}\text{Np}$  (re.,  $\varnothing 0.5 \times 10$  cm vs.  $\varnothing 0.7 \times 5$  cm in Fig. 2d).

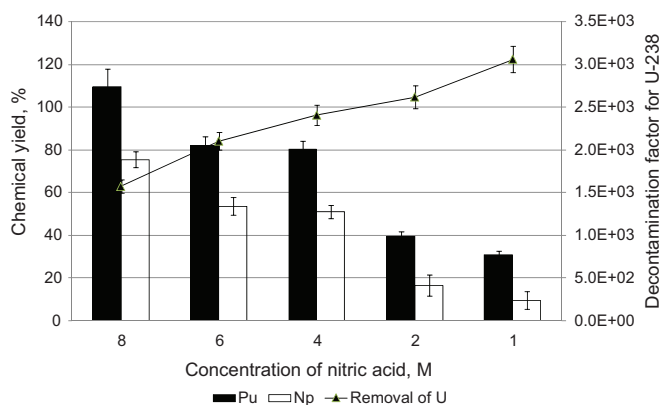
To further improve the decontamination factors of  $^{238}\text{U}$ , varied concentrations of nitric acid and flow rates were investigated in the isolation of  $^{237}\text{Np}$  onto AG 1- $\times$ 4 resin using 10 g of Danish soil as

a sample. Experimental results (see Fig. 4) demonstrated that the lower the concentration of nitric acid, the better the decontamination factor for U. However, chemical yields of  $^{242}\text{Pu}$  and  $^{237}\text{Np}$  as well as the ratio thereof dropped dramatically with the decrease in the concentration of nitric acid, which makes low concentration of nitric acid impracticable in the rinsing step due to significant losses of target radionuclides. An 8 M  $\text{HNO}_3$  solution was thus chosen for the remainder of the work, which is in a good agreement with previously published works [7,25,26]. To evaluate the applicability of the analytical protocol proposed, measurement of the background signal at  $m/z = 237$  was carried out with increasing concentrations of  $^{238}\text{U}$ . Within the concentration range tested (10–1000 ng l<sup>-1</sup>  $^{238}\text{U}$ ), the background signal barely changed, thereby confirming the reliability of the protocol for  $^{237}\text{Np}$  assays at environmentally relevant concentration levels. When high concentrations of thorium are not removed from the sample, an interfering signal at  $m/z = 242$  which



**Fig. 3.** Variation of decontamination factors for uranium on the basis of column dimensions and anion exchanger type (sample: 10 g of Danish soil; Flow rate: 1.0 mL min<sup>-1</sup> for sample loading and 2.5 mL min<sup>-1</sup> for column rinsing and elution).





**Fig. 4.** Effect of the concentration of nitric acid on the removal of uranium from AG 1-×4 (50–100 mesh) (sample: 10 g of Danish soil; separation protocol: column rinsing with 100 ml of a given concentration of  $\text{HNO}_3$  followed by 100 ml of 9 M HCl, elution of  $^{237}\text{Np}$  and  $^{242}\text{Pu}$  with 40 ml of 0.5 M HCl. Flow rate:  $1.0 \text{ ml min}^{-1}$  for sample loading and  $2.5 \text{ ml min}^{-1}$  for column rinsing and elution).

is caused by the polyatomic ion  $^{230}\text{Th}^{12}\text{C}$  might overlap with  $^{242}\text{Pu}$ . To minimize Th interfering effect, a 9 M HCl rinsing step was hence adopted after 8 M  $\text{HNO}_3$  washing, rendering decontamination factors up to  $10^4$ – $10^5$  for Th.

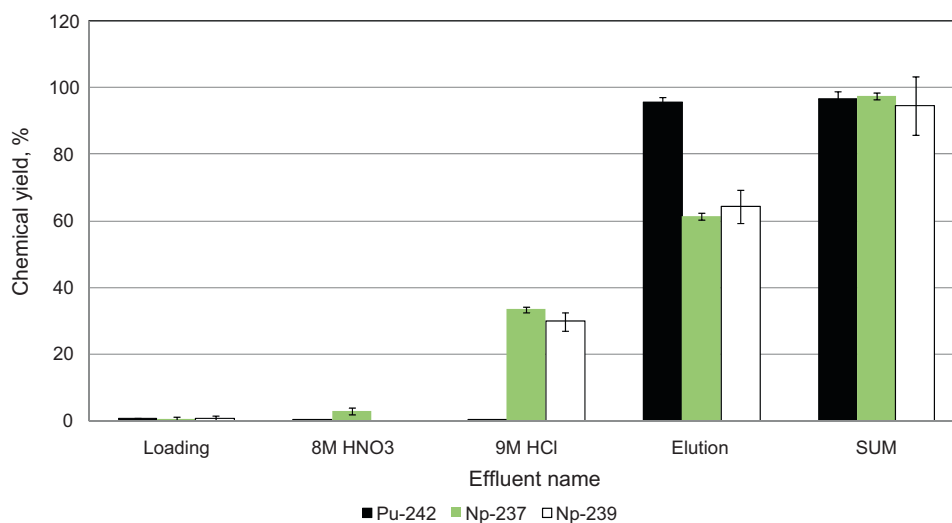
Flow rates for the two-step rinsing were varied from  $2.5$  to  $5.0 \text{ ml min}^{-1}$  aimed at increasing the sample throughput and improving the analytical efficiency. At  $5.0 \text{ ml min}^{-1}$  the chemical yields of  $^{242}\text{Pu}$  and  $^{237}\text{Np}$  were relatively low, therefore, the washing and elution flow rates were affixed to  $2.5 \text{ ml min}^{-1}$ . The sample loading flow rate was however set to  $1.0 \text{ ml min}^{-1}$  to ensure quantitative uptake of  $^{242}\text{Pu}$  and  $^{237}\text{Np}$ .

### 3.2. Suitability of $^{242}\text{Pu}$ as a tracer for Np determination

Experimental results compiled in Figs. 2 and 4 demonstrated that losses of  $^{237}\text{Np}$  were still significant (ca. 20–30%) whenever  $^{242}\text{Pu}$  was quantitatively retrieved from the sample under all investigated experimental conditions. Further experiments were therefore designed to unravel the physicochemical behavior of Np and Pu onto AG 1-×4 utilizing 10 g of soil spiked with a given amount of  $^{237}\text{Np}$ ,  $^{239}\text{Np}$  and  $^{242}\text{Pu}$ . All effluents from the column

separation procedure were collected and measured for  $^{239}\text{Np}$  using gamma spectrometry while  $^{237}\text{Np}$  and  $^{242}\text{Pu}$  were quantified by ICP-MS.  $^{239}\text{Np}$  was added to the sample for better ascertainment of the fate of Np during the overall chemical separation procedure since effluents from sample loading and column rinsing might contain high amounts of interfering species deteriorating the reliable ICP-MS quantification of  $^{237}\text{Np}$ . Fig. 5 compiles the overall results as obtained from four assay replicates of 10 g of Danish soil. No appreciable losses of  $^{242}\text{Pu}$  were observed during sample loading and column rinsing using 8 M  $\text{HNO}_3$  and 9 M HCl, respectively, while  $30 \pm 5\%$  of  $^{237}\text{Np}$  (and  $^{239}\text{Np}$ ) was found in the 9 M HCl fraction. The discrepancies in chemical yields between  $^{237}\text{Np}$  (or  $^{239}\text{Np}$ ) and  $^{242}\text{Pu}$  are therefore caused by the loss of  $^{237}\text{Np}$  (or  $^{239}\text{Np}$ ) occurring in the 9 M HCl rinsing step. Published values for distribution coefficients of Pu and Np on anion exchangers in HCl media indicate a slightly higher affinity for Pu relative to Np [25], which might be accentuated when operating in a dynamic flow-through mode in lieu of steady-state conditions. The loss of Np might also be encountered during the on-column transformation of nitrate complexes of Np(IV) and Pu(IV) into their chloride complexes, because the stability of chloride complexes of Pu might be better than those of Np. Oxidation of Np to the pentavalent oxidation state is yet another possibility and should in this case be mediated by some intermediate product formed when mixing nitric and hydrochloric acids on-column. In principle, the valence state change of Np during 9 M HCl rinsing step might be detected with spectrophotometry at sufficiently high concentration, but unfortunately standards with the high concentration of Np are not readily available for the authors.

Interestingly, the cumulative losses of Np followed a linear correlation against the volume of 9 M HCl from 20 ml and onwards up to 100 ml. This effect has not been earlier discussed in the literature in the use of AG 1-type resins for the uptake and isolation of Np. This linear correlation reveals a constant bleeding of Np from the anion exchanger in a dynamic flow-through mode, which might be a consequence of the lower distribution coefficients of Np chlorocomplexes onto gel-type anion exchange resins as compared with Pu chlorocomplexes. The losses of Np could be thus minimized by reducing the volume of 9 M HCl. Repeated assays exploiting 2 ml of AG 1-×4 (50–100 mesh) for 10 g of Danish soil however demonstrated a relatively steady  $^{237}\text{Np}/^{242}\text{Pu}$  chemical yield ratio with an average value of  $0.67 \pm 0.04$  ( $n = 15$ ) when using 100 ml of 9 M HCl for column rinsing. This implies that under well-

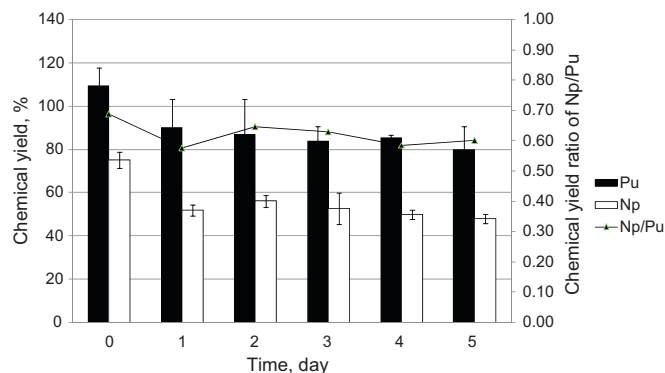


**Fig. 5.** Breakdown of  $^{237}\text{Np}$ ,  $^{239}\text{Np}$  and  $^{242}\text{Pu}$  chemical yields in different fractions of the overall steps in the SI-column separation protocol (sample: 10 g of Danish soil; resin: AG 1-×4 (50–100 mesh); separation protocol: column rinsing with 100 ml of 8 M  $\text{HNO}_3$  followed by 100 ml of 9 M HCl, elution of  $^{237}\text{Np}$  and  $^{242}\text{Pu}$  with 40 ml of 0.5 M HCl. Flow rate:  $1.0 \text{ ml min}^{-1}$  for sample loading and  $2.5 \text{ ml min}^{-1}$  for column rinsing and elution).

**Table 1**Determination of  $^{237}\text{Np}$  activity in reference materials and spiked environmental samples using the proposed SI method in combination with ICP-MS.

Sample	Amount (g)	$^{237}\text{Np}$ spiked (mBq)	Measured activity of $^{237}\text{Np}$ ( $\text{Bq kg}^{-1}$ )	Literature or expected activities of $^{237}\text{Np}$ , ( $\text{Bq kg}^{-1}$ )
IAEA-135 sediment	1.0	–	$0.93 \pm 0.05$ (2.91)	$0.846 \pm 0.045$ [21]
Irish sea sediment	1.0	–	$0.99 \pm 0.04$ (0.13)	$0.987 \pm 0.048$ [7]
Spiked Danish soil	10	$0.50 \pm 0.02$	$0.049 \pm 0.003$ (0.58)	$0.050 \pm 0.002$
Spiked Danish seaweed	20	$0.50 \pm 0.02$	$0.026 \pm 0.002$ (0.87)	$0.025 \pm 0.001$

Results are expressed as the mean of four replicates  $\pm$  standard deviation. Numbers in brackets are  $|t|_{\text{exp}}$  values, at the 95% confidence interval, the critical  $t$ -value ( $t_{\text{crit}}$ ) is 3.18 for  $n = 4$ .



**Fig. 6.** Temporal stability of Pu(IV) and Np(IV) in the sample loading solution containing 8 M  $\text{HNO}_3$  at  $3^\circ\text{C}$  (sample: 10 g of Danish soil; resin: AG 1- $\times$ 4 (50–100 mesh); separation protocol: column rinsing with 100 ml of 8 M  $\text{HNO}_3$  followed by 100 ml of 9 M  $\text{HCl}$ , elution of  $^{237}\text{Np}$  and  $^{242}\text{Pu}$  with 40 ml of 0.5 M  $\text{HCl}$ . Flow rate:  $1.0 \text{ ml min}^{-1}$  for sample loading and  $2.5 \text{ ml min}^{-1}$  for column rinsing and elution).

defined experimental conditions as provided by SI manifolds,  $^{242}\text{Pu}$  should be regarded as a viable tracer for  $^{237}\text{Np}$  chemical yield monitoring.

### 3.3. Temporal stability of Pu(IV) and Np(IV) in the sample loading solution

In our previous work [22], we compared various methods for valence adjustment and stabilization of Pu(IV) and Np(IV). The redox pair  $\text{K}_2\text{S}_2\text{O}_5$ –8 M  $\text{HNO}_3$  was proven the most effective reagent for simultaneous valence adjustment to Pu(IV) and Np(IV). The stability of Pu(IV) and Np(IV) in this solution is of major importance when preparing several samples to be analysed with the aid of an automated method where samples are not run in parallel. The valence states for both elements should be kept unaffected until the last sample has been loaded onto the column. To determine the time span to which Pu(IV) and Np(IV) are stable in the sample loading milieu, we conducted tests employing  $\text{K}_2\text{S}_2\text{O}_5$ –8 M  $\text{HNO}_3$  redox reagents and keeping the sample loading solution in 8 M  $\text{HNO}_3$  at  $3^\circ\text{C}$ . The experimental results (see Fig. 6) reveal that Pu(IV) and Np(IV) could be stabilized in an 8 M  $\text{HNO}_3$  medium for up to 5 days at  $3^\circ\text{C}$  since the  $^{237}\text{Np}/^{242}\text{Pu}$  chemical yield ratios were relatively constant in the range of 0.6–0.7, with no statistically significant differences in chemical yields at the 95% confidence.

It should be noted that remarkable decreases in chemical yields of Pu and Np were observed for the samples kept under  $3^\circ\text{C}$  for 1–5 days compared with the ones immediately loaded onto the column after valence adjustment. This might be a consequence of lower distribution coefficients of Pu and Np onto the anion exchanger under lower reaction temperature, because those sample solutions were not re-warmed up to room temperature before loading onto the column.

### 3.4. Application of the proposed SI-separation method to environmental solid analysis

To explore the potential applicability of the present method for  $^{237}\text{Np}$  determination in a variety of environmental solids, analyses were performed on a standard reference material (IAEA-135 sediment), an in-house reference sample (Irish Sea sediment) and spiked seaweed and soil samples. The analytical results are listed in Table 1. A good agreement was found for all samples between experimental results and literature reported, certified or estimated values, suggesting the applicability of the proposed method for the determination of  $^{237}\text{Np}$  when utilizing  $^{242}\text{Pu}$  as a non-isotopic tracer combined with the use of a normalization coefficient (viz., 0.67) for calculation of actual chemical yields of  $^{237}\text{Np}$ .

On-column separation of a single sample in this work could be accomplished within 2.5 h, thus nine samples can be sequentially processed in a fully automated mode within one day. Because of the automation of column separation, sample treatment and chromatographic separation are allowed to be undertaken in parallel for a given number of samples, which is otherwise not straightforward (e.g., in the conventional methods). There are three distinctive benefits of using a fast automated separation procedure capitalized on SI when analysing  $^{237}\text{Np}$ . First, the improved sample throughput compared with manual separation methods fosters Pu and Np to be preserved as Pu(IV) and Np(IV), respectively, in the course of the assays. Secondly, the rapid separation in the automated procedure also opens the possibility of utilization of the short-lived  $^{239}\text{Np}$  as isotopic tracer. Last but not least, the automated processing of samples in a programmable sequence leads to improved reproducibility, decrease of measurement uncertainty, minimization of sample cross-contamination and improved safety due to minimum analyst intervention in the overall column separation procedure.

## 4. Conclusion and outlook

A flow-based anion exchange method was developed in this work for the determination of  $^{237}\text{Np}$  at environmentally relevant levels. The detection of target radionuclides was performed using ICP-MS, offering advantages over alpha spectrometry of expeditious assays and low detection limits. The analytical results herein reported for  $^{237}\text{Np}$  assays using AG 1- $\times$ 4-type anion exchangers nested to a multi-position valve of the SI setup demonstrate that  $^{237}\text{Np}$  to  $^{242}\text{Pu}$  chemical yield ratios were almost steady within the range of 0.6–0.7 under certain experimental conditions. Although losses of Np occurred during column separation, the good agreement between experimental results and expected values for  $^{237}\text{Np}$  in reference materials and spiked real-life samples reveals that  $^{242}\text{Pu}$  is suitable as a non-isotopic tracer for  $^{237}\text{Np}$  provided that normalization is taken into account.

Further work is underway to improve the chemical yields of  $^{237}\text{Np}$  via multivariate optimization of the overall analytical procedure. A simple means to alleviate differences in chemical yields of Np and Pu is to decrease the volume of rinsing 9 M  $\text{HCl}$  yet at expenses of increased amounts of Th in the eluate. Whenever not feasible, alternative anion exchange resins, e.g., macro-porous AG

MP-1 M, might be evaluated as well as the modulation of chemical composition of the washing solution via addition of a redox reagent, such as NaNO<sub>2</sub>, to prevent the on-column changeover of Np(IV).

## Acknowledgements

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## Paper VI

Qiao, J. X., Hou, X. L., Roos, P., Miró, M. High-throughput Sequential Injection Method for Simultaneous Determination of Plutonium and Neptunium in Environmental Solids Using Macro-porous Anion Exchange Chromatography followed by Inductively Coupled Plasma Mass Spectrometric Detection. *Analytical Chemistry*. 2011, 83, 374-381.



# High-Throughput Sequential Injection Method for Simultaneous Determination of Plutonium and Neptunium in Environmental Solids Using Macroporous Anion-Exchange Chromatography, Followed by Inductively Coupled Plasma Mass Spectrometric Detection

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This paper reports an automated analytical method for rapid and simultaneous determination of plutonium and neptunium in soil, sediment, and seaweed, with detection via inductively coupled plasma mass spectrometry (ICP-MS). A chromatographic column packed with a macroporous anion exchanger (AG MP-1 M) was incorporated in a sequential injection (SI) system for the efficient retrieval of plutonium, along with neptunium, from matrix elements and potential interfering nuclides. The sorption and elution behavior of plutonium and neptunium onto AG MP-1 M resin was compared with a commonly utilized AG 1-gel-type anion exchanger. Experimental results reveal that the pore structure of the anion exchanger plays a pivotal role in ensuring similar separation behavior of plutonium and neptunium along the separation protocol. It is proven that plutonium-242 ( $^{242}\text{Pu}$ ) performs well as a tracer for monitoring the chemical yield of neptunium when using AG MP-1 M resin, whereby the difficulties in obtaining a reliable and practicable isotopic neptunium tracer are overcome. An important asset of the SI setup is the feasibility of processing up to 100 g of solid substrates using a small-sized (ca. 2 mL) column with chemical yields of neptunium and plutonium being  $\geq 79\%$ . Analytical results of three certified/standard reference materials and two solid samples from intercomparison exercises are in good agreement with the reference values at the 0.05 significance level. The overall on-column separation can be completed within 3.5 h for 10 g of soil samples. Most importantly, the anion-exchange mini-column suffices to be reused up to 10-fold with satisfactory chemical yields ( $> 70\%$ ), as demanded in environmental monitoring and emergency scenarios, making the

proposed automated assembly well-suited for unattended and high-throughput analysis.

Plutonium (Pu) and neptunium (Np) were released into the environment by nuclear activities including the nuclear weapons testing from the 1940s to the 1980s, nuclear accidents and discharges from nuclear power plants, and spent nuclear fuel reprocessing plants.<sup>1</sup> They are regarded as highly radiologically and biologically hazardous pollutants in the environment, because of alpha emission and long half-lives of their most important isotopes (e.g.,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ , and  $^{237}\text{Np}$ ), respectively. From the viewpoint of environmental risk assessment and radiological emergency preparedness, as well as nuclear waste treatment, there is a current requirement in accurate determination of Pu and Np in various environmental compartments.<sup>2</sup>

In principle, it is possible to perform simultaneous isolation of Pu and Np, because the chemical behaviors of tetravalent Pu and Np anionic complexes are similar in nitric and hydrochloric acid media.<sup>3,4</sup> Plutonium isotopes (viz.,  $^{242}\text{Pu}$ ,  $^{236}\text{Pu}$ , or  $^{244}\text{Pu}$ ) might be selected as nonisotopic tracers to monitor the chemical yield of Np. The remarkable advantage would be the avoidance of difficulties in obtaining isotopic Np tracers ( $^{239}\text{Np}$ ,  $^{236}\text{Np}$ , or  $^{235}\text{Np}$ ), which are not commercially available and are not easily produced and purified in most laboratories.<sup>5,6</sup> Moreover, the analytical time would be shortened, because there would be no need for chemical separation of Np (namely,  $^{237}\text{Np}$ ) from Pu, and the consumption of samples and chemicals would also be reduced to a large extent. A handful of analytical methods have

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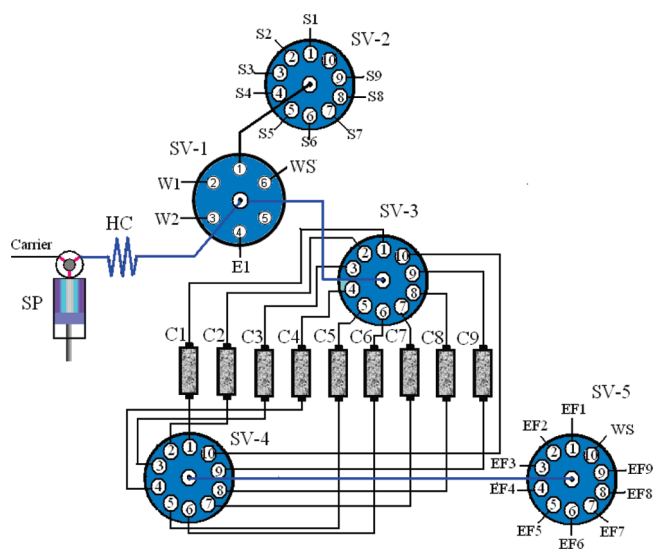
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been reported to date for the simultaneous determination of Pu and Np in environmental samples;<sup>5–10</sup> however, only a few works have exploited a Pu isotope as a tracer for both Pu and Np.<sup>5,7,10</sup>

Difficulties in using Pu isotopes as tracers for <sup>237</sup>Np determination might arise from the fact that the tetravalent Np (Np(IV)), being easily oxidized, may behave differently from Pu(IV) onto the sorptive resin during separation. The first application of extraction chromatography (TEVA) for the simultaneous separation of Pu and Np, using a Pu isotopic tracer, was reported by Kim et al., but it was only devoted to small-sized samples ( $\leq 4$  g of soil).<sup>10</sup> In our previous work, larger-sized samples (10 g of soil) were successfully analyzed for Pu and Np using a TEVA column,<sup>5</sup> but chemical yields, in some instances, were  $<60\%$ , as a consequence of the low distribution coefficients of Pu and Np onto TEVA in highly concentrated nitric acid.<sup>11</sup> Compared with extraction chromatography, anion-exchange chromatography is cost-effective and has widespread use in routine radiochemical assays. AG 1 gel-type (also called microporous) resins are the sorbent of choice and are commonly utilized for the anion-exchange separation of Pu and/or Np in a variety of analytical protocols.<sup>7,12–22</sup> Large-sized gel-type (AG 1-X4) anion-exchange columns have also been exploited for simultaneous isolation of Pu and Np, using <sup>242</sup>Pu as a tracer;<sup>7</sup> yet, the procedure is tedious and operated in a manual fashion, so it is time-consuming and labor-intensive. Moreover, our previous investigation, implementing AG 1-gel-type exchangers in a flow-based network for the dynamic separation of <sup>237</sup>Np using <sup>242</sup>Pu as a nonisotopic tracer, revealed poor chemical yields for Np.<sup>6</sup>

For the purpose of developing a high-throughput analytical method for simultaneous determination of Pu isotopes (namely, <sup>239</sup>Pu and <sup>240</sup>Pu) and <sup>237</sup>Np, a paradigm shift is proposed in this work, to exploit macroporous anion exchangers, which have been barely used in radiochemical assays. To our best



**Figure 1.** Schematic diagram of the sequential injection (SI) anion-exchange column manifold for simultaneous determination of Pu and Np in environmental solids. W1, 8 mol/L HNO<sub>3</sub>; W2, 9 mol/L HCl; E1, 0.5 mol/L HCl; WS, waste; S1–S9, ports for sample loading; EF1–EF9, ports for eluate collection; SP, syringe pump; SV-1–SV-5, selection valves; HC, holding coil; and C1–C9, nine anion-exchange columns.

knowledge, this is the first automated flow-based method using macroporous anion-exchange column separation for concurrent determination of trace levels of Pu and Np in environmental solid samples (viz., soil, sediment, and seaweed).

## EXPERIMENTAL SECTION

**Flow-Based Setup.** The automated separation setup consisted of an FIALab-3500B sequential injection (SI) system (FIALab Instruments, Bellevue, WA) that was furnished with the following: a syringe pump (SP, Cervo, Sunnyvale, CA, 25 mL capacity); one 6-port multiposition selection valve (SV-1); four 10-port multiposition section valves, identified as SV-2 to SV-5 (Valco Instruments, Houston, TX); and nine anion-exchange columns. A schematic illustration of the SI analyzer is shown in Figure 1. Within the system, nine samples can be sequentially processed by computer control via FIALab-associated software. All the outlets of the selection valve (SV-1) were connected through PEEK ferrules with rigid poly tetrafluoroethylene (PTFE) tubing (2.4 mm inner diameter (id)/3.2 mm outer diameter (od)), and all the outlets of the external selection valves (SV-2 to SV-5) were connected through PEEK ferrules with rigid PTFE tubing of smaller diameter (0.8 mm id/1.6 mm od). The central port of the SV-1 was connected to the holding coil (HC), which consisted of a 6.6-m-long PTFE tubing with an inner capacity of 30 mL (2.4 mm id/3.2 mm od). Hereby, it should be mentioned that two of the external selection valves, i.e., SV-2 and SV-5, might be replaced by an autosampler and eluate autocollector, respectively.

**Standards, Reagents, and Samples.** All reagents used in the experiment were analytical reagent grade and prepared using deionized water (18 MΩ·cm). A <sup>242</sup>Pu standard solution (0.1037 Bq/g in 2 mol/L HNO<sub>3</sub>) diluted from NBL-CRM 130 (New Brunswick Laboratory, Argonne, IL) was used as a chemical yield tracer for both Pu and Np. <sup>237</sup>Np (0.01175 Bq/g in 2 mol/L HNO<sub>3</sub>) and <sup>239</sup>Pu solutions (0.100 Bq/g in 2 mol/L HNO<sub>3</sub>) were

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supplied by Risø National Laboratory for Sustainable Energy (Denmark). Standard solutions of uranium and thorium were purchased from NIST (Gaithersburg, MD).

The anion-exchange resins explored in this work were AG MP-1 M macroporous resins with particle sizes of 50–100 and 100–200 mesh, as well as AG 1-X4 gel-type resin with particle size of 100–200 mesh, both in chloride form (Bio Rad Laboratories Inc., Hercules, CA). AG MP-1 resin is the macroporous equivalent of AG 1-gel-type resin with an effective surface area of ca. 23 m<sup>2</sup>/g and porosity as large as 20%. The resin was swelled in deionized water and poured into a ca. 2 mL (5 mm id × 10 cm long) Econo-column (Bio Rad Laboratories, Inc.) and preconditioned with an 8 mol/L HNO<sub>3</sub> solution. Three certified reference materials including two sediments (IAEA-385 and IAEA-135), and one seaweed (NIST-4359), and two reference materials from a laboratory round-robin intercomparison (namely, a Danish soil<sup>23</sup> and an Irish Sea sediment) were employed to evaluate the trueness of the method. Unless otherwise stated, the Danish soil was selected for method development.

**Sample Pretreatment.** A certain amount (0.5–100 g, depending on the concentration of Pu and Np) of a given solid sample was placed in a beaker and ashed at 550 °C overnight to decompose the organic matter. The sample was spiked with 5 mBq of <sup>242</sup>Pu as a tracer. With regard to the Danish soil, 0.5 mBq of <sup>237</sup>Np was added to increase the signal of <sup>237</sup>Np in ICP-MS measurement, because of the negligible concentration of <sup>237</sup>Np in the original sample. Aqua regia was then added to the sample (in a ratio of 10 mL of aqua regia to 1 g of sample) and the mixture was digested on a hot plate at 150 °C for 30 min and then 200 °C for 2 h, respectively. During the digestion, the beaker was covered with a watchglass, to prevent significant evaporation of the solution. After cooling, the supernatant was filtered through a GF/A filter into a centrifuge tube, and the beaker and filter paper were washed with 30 mL of 0.2 mol/L HCl. Concentrated ammonia was added to the supernatant to adjust the pH to a value of 8–9, to coprecipitate Pu and Np with iron hydroxides and remove concomitant matrix components, whereupon the coprecipitate was separated by centrifugation. For small-sized samples (e.g., ≤ 1 g soil or sediment), the overall Np must be adjusted to a tetravalent state with K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> prior to the above step, to ensure the quantitative precipitation of Np, because of potential losses of the target radionuclide, as a consequence of the relatively high solubility of Np(V). Thirty milliliters (30 mL) of 6 mol/L NaOH was added to the coprecipitate to dissolve amphoteric elements, such as aluminum and vanadium, and then remove them by centrifugation.

A few milliliters of concentrated HCl were added to dissolve the precipitate from the pretreatment step above, and then 300 mg of K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> was added to convert the overall Pu and Np to Pu(III) and Np(IV), respectively. NaOH (6 mol/L) was added to the solution to adjust the pH to a value of 10. After centrifugation, a few milliliters of concentrated HCl were added to dissolve the resulting precipitate. Concentrated HNO<sub>3</sub> was then added to oxidize Pu(III) to Pu(IV), and, finally, the solution

was adjusted to 8 mol/L HNO<sub>3</sub> to stabilize the target species as Pu(IV) and Np(IV) prior to injection into the SI setup.

For large sample sizes (viz., 20 g of seaweed and 20–100 g of soil), the sample was initially divided into 2–10 aliquots with a mass of 10 g each to facilitate separation of analytes by coprecipitation. Pretreatment of the aliquots was performed simultaneously in a batchwise approach. After pretreatment, subsample solutions were combined and the composite sample was subjected to the automated column separation.

**Automated Separation Scheme.** The SI anion-exchange chromatographic procedure consists of the following five steps:

(I) Rinse the holding coil with 50 mL of deionized water and wash the sample inlet and manifold tubing with 8 mol/L HNO<sub>3</sub> at a flow rate of 10 mL/min;

(II) Precondition the anion-exchange resin with 20 mL of 8 mol/L HNO<sub>3</sub> at a flow rate of 2.4 mL/min;

(III) Load the sample (from 15 to 150 mL, depending on the sample size (e.g., 15 mL for 10 g of Danish soil)) in a 8 mol/L HNO<sub>3</sub> medium onto the anion-exchange column;

(IV) Rinse the column with 80 mL of 8 mol/L HNO<sub>3</sub> to remove most of the uranium and matrix elements, followed by 60 mL of 9 mol/L HCl to remove thorium; and

(V) Elute Pu and Np with 40 mL of 0.5 mol/L HCl.

Unless otherwise stated, the flow rate for the overall column separation procedure was 1.2 mL/min. In case the anion-exchange column is reused, 60 mL of 0.05 mol/L H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> is used for column cleanup between samples.

The eluate was evaporated to dryness on a hot plate to eliminate HCl. The residue was redissolved in 5 mL of 0.5 mol/L HNO<sub>3</sub>, and the reconstituted solution was analyzed by inductively coupled plasma mass spectroscopy (ICP-MS) for quantification of the Pu isotopes and <sup>237</sup>Np and interfering elements, such as U, Th, and Pb.

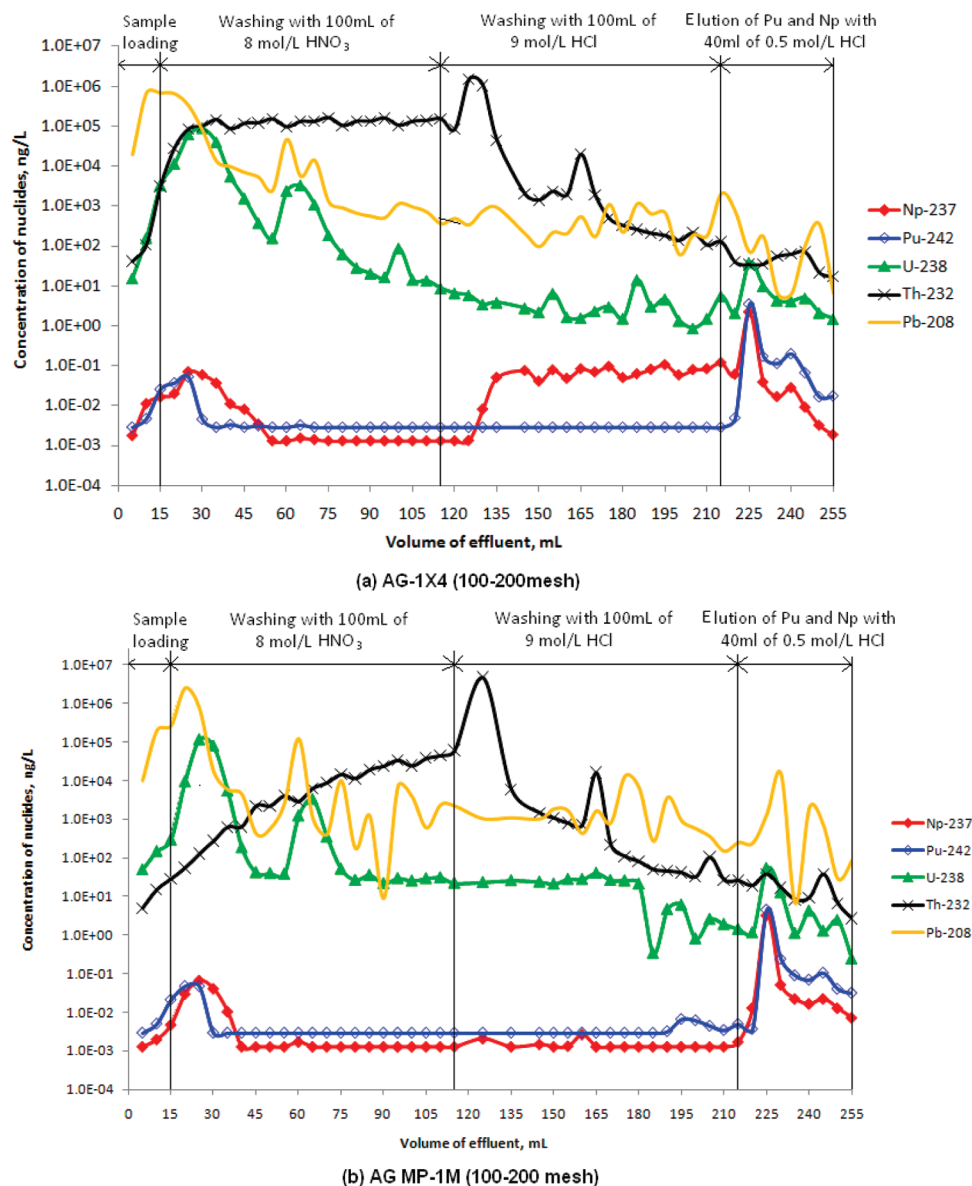
**Determination of Plutonium and Neptunium Using ICP-MS.** Prior to sample measurement, the ICP-MS instrument was tuned using a 1.0 µg/L solution of <sup>238</sup>U in 0.5 mol/L HNO<sub>3</sub>. The typical operational conditions of the instrument have been given elsewhere.<sup>5,24</sup> Note that the instrumental parameters were optimized each time the instrument was initialized. Typical sensitivities of plutonium (i.e., <sup>239</sup>Pu, <sup>240</sup>Pu, and <sup>242</sup>Pu) and neptunium (<sup>237</sup>Np) ranged from 2 × 10<sup>5</sup> to 4 × 10<sup>5</sup> cps per µg/L.<sup>5</sup>

To 5 mL of processed sample solution in 0.5 mol/L HNO<sub>3</sub>, 50.0 µL of 100 µg/L In(III) (in the form of InCl<sub>3</sub>) was added as an internal standard. The concentrations of <sup>239</sup>Pu, <sup>240</sup>Pu, <sup>242</sup>Pu, and <sup>237</sup>Np, as well as <sup>238</sup>U, <sup>232</sup>Th, and <sup>208</sup>Pb, were determined using an ICP-MS system (X Series<sup>II</sup>, Thermo Fisher Scientific, Waltham, MA) that was equipped with an Xs-skimmer cone and a concentric nebulizer under hot plasma conditions. <sup>239</sup>Pu and <sup>237</sup>Np standard solutions were prepared in 0.5 mol/L HNO<sub>3</sub> containing 1.0 µg/L In(III). Detection limits, calculated as three times of the standard deviations (3σ) of the processing blank, were 1.5 pg/L for <sup>239</sup>Pu, <sup>240</sup>Pu, <sup>242</sup>Pu, and <sup>237</sup>Np. A 0.5 mol/L HNO<sub>3</sub> solution was used as a washing solution between consecutive assays. No carry-over effects were observed for consecutive analysis of samples differing in Pu and Np concentration by up to 3 orders of magnitude. The

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**Figure 2.** Sorption and elution behavior of Pu, Np, U, Th, and Pb on different anion exchangers: (a) gel-type anion exchanger AG 1-X4 (100–200 mesh) and (b) macroporous anion exchanger AG MP-1 M (100–200 mesh). (Sample = 10 g of Danish soil, flow rate in the entire procedure = 1.2 mL/min.)

regression line was proven to be linear over the range of 0.01 ng/L to 100 ng/L for both Pu and Np.

*CAUTION! Safety concerns in handling radioactive nuclides of Pu and Np should be stressed here. In this work, a semihot laboratory was specifically used for storage of the radioactive stock solutions, and care was taken whenever samples were spiked with radionuclides of Pu and Np and the spikes were measured gravimetrically.*

## RESULTS AND DISCUSSION

**Comparison of the Analytical Performance of Macroporous AG MP-1 M against Gel-Type AG 1-X4 for Isolation of Target Species.** To the best of our knowledge, no studies have yet compared, in detail, the analytical performance of macroporous anion exchangers with gel-type resins for simultaneous determination of Pu isotopes and <sup>237</sup>Np in environmental solid samples. In this work, 10 g of Danish soil spiked with ca. 5 mBq of <sup>242</sup>Pu and 0.5 mBq of <sup>237</sup>Np was used to investigate the influence of

resin type on the separation efficiency. The sorption and elution profiles of Pu, Np, U, Th, and Pb onto anion exchangers are shown in Figure 2a and 2b for the gel-type anion exchanger AG 1-X4 (100–200 mesh) and macroporous AG MP-1 M (100–200 mesh), respectively. The contents of <sup>242</sup>Pu and <sup>237</sup>Np in the four fractions collected from the column separation procedure, including sample loading, rinsing with 8 M HNO<sub>3</sub> and 9 M HCl, and elution with 0.5 M HCl, are summarized in Table 1. With regard to the gel-type AG 1-X4, minute amounts (<5%) of <sup>242</sup>Pu and <sup>237</sup>Np were observed in either the sample loading or the 8 M HNO<sub>3</sub> rinsing fractions. However, ~20% of <sup>237</sup>Np was lost in the 9 M HCl rinsing fraction. As a result, a notable difference between the chemical yields of <sup>242</sup>Pu (60.6%) and <sup>237</sup>Np (45.4%) in the eluate was detected with a <sup>237</sup>Np/<sup>242</sup>Pu chemical yield ratio of 0.75, which is consistent with our previous investigations.<sup>6</sup>

**Table 1. Comparison of the Distribution of  $^{242}\text{Pu}$  and  $^{237}\text{Np}$  in Various Stages of the SI-Based Analytical Procedure Exploiting AG 1-X4 and AG MP-1M Anion Exchangers<sup>a</sup>**

step	AG 1-X4 Resin (100–200 mesh)		AG MP-1 M Resin (100–200 mesh)	
	$^{242}\text{Pu}$ (%)	$^{237}\text{Np}$ (%)	$^{242}\text{Pu}$ (%)	$^{237}\text{Np}$ (%)
sample loading	$0.5 \pm 0.1$	$0.6 \pm 0.1$	$1.0 \pm 0.1$	$0.4 \pm 0.1$
8 M $\text{HNO}_3$ rinsing	$2.2 \pm 0.1$	$4.3 \pm 0.2$	$2.3 \pm 0.1$	$3.4 \pm 0.2$
9 M $\text{HCl}$ rinsing	$1.3 \pm 0.1$	$23.6 \pm 1.2$	$0.4 \pm 0.1$	$0.2 \pm 0.1$
elution	$60.6 \pm 3.0$	$45.4 \pm 2.3$	$79.3 \pm 4.0$	$82.6 \pm 4.1$
SUM	$64.5 \pm 3.2$	$73.9 \pm 3.7$	$83.0 \pm 4.1$	$86.6 \pm 4.3$

<sup>a</sup> All values are the average of two replicates  $\pm$  uncertainty.

On the other hand, minute amounts ( $\leq 4\%$ ) of  $^{242}\text{Pu}$  and  $^{237}\text{Np}$  were concurrently found in the sample loading and rinsing steps when using the AG MP-1 M anion exchanger. Most importantly, the chemical yields of  $^{242}\text{Pu}$  (79.3%) and  $^{237}\text{Np}$  (82.6%) in the elution were significantly improved with a  $^{237}\text{Np}/^{242}\text{Pu}$  chemical yield ratio of 1.04. This means  $^{242}\text{Pu}$  performs well as a tracer for monitoring the chemical yield of  $^{237}\text{Np}$ . Note that the summation of  $^{242}\text{Pu}$  and  $^{237}\text{Np}$  chemical yields in the four fractions of the separation procedure is  $<100\%$ , yet better in the AG MP-1 M anion exchanger (see Table 1), which should be a consequence of the loss in sample pretreatment, sample reconstitution prior to ICP-MS measurement and/or remains of target analytes in the anion-exchange column that were not completely eluted with 40 mL of 0.5 M  $\text{HCl}$ .

Although AG 1-X4 resin has a nominal anion-exchange capacity identical to that of AG MP-1 M (1.0 meq/mL), AG 1-X4 beads are characterized by a dense internal structure with no discrete pores, in contrast with AG MP-1 M beads, which bear a porous, multichannelled structure.<sup>25</sup> Experimental results stated above and compiled in Figure 2 reveal that pore structure—and, thus, bead permeability—plays a remarkable role in the sorption and elution behavior of Np. Pre-elution of Np in 9 M  $\text{HCl}$  on AG 1-X4 resin might arise from the fact that less-functional moieties remain available in a dynamic flow-through solid-phase extraction mode, compared with AG MP-1M, and the lower distribution coefficients of  $^{237}\text{Np}$  chlorocomplexes onto anion-exchange beads as compared with that of Pu chlorocomplexes.<sup>3,25</sup> Figure 2 also shows that potential interfering nuclides (including U, Th, and Pb) behave similarly on both anion exchangers. In fact, both U and Pb could be quantitatively removed from the columns with 8 M  $\text{HNO}_3$ , whereas Th could be removed with 9 M  $\text{HCl}$ . In the eluate, the decontamination factors for U and Th were in the range of  $10^3$ – $10^4$  and  $10^4$ – $10^5$ , respectively, while those of Pb varied widely, from  $1 \times 10^3$  to  $1 \times 10^6$ , because of external contamination from the vessels and reagents. However, no severe interferences from U, Th, and Pb in the ICP-MS measurement of Pu isotopes and  $^{237}\text{Np}$  in the SI eluates were detected in any case.

**Effect of Particle Size and Flow Rate.** Because resins with large particle size could be compatible with high flow rates and, therefore, expedite sample analysis, the effects of particle size and flow rate on the separation efficiency were investigated and summarized in Table 2. The analytical comparison of two particle-size distributions (50–100 mesh and 100–200 mesh) of AG MP-1

**Table 2. Effect of Particle Size and Flow Rate on the Separation Efficiency of AG MP-1M in an SI-Based Mode<sup>a</sup>**

particle size (mesh)	flow rate (mL/min)	Chemical Yield		
		$^{242}\text{Pu}$ , %	$^{237}\text{Np}$ , %	$^{237}\text{Np}/^{242}\text{Pu}$ ratio
50–100	1.2	$73.6 \pm 3.8$	$70.2 \pm 4.2$	0.95
100–200	1.2	$84.7 \pm 4.5$	$82.3 \pm 5.1$	0.97
100–200	2.4	$75.6 \pm 5.0$	$62.2 \pm 4.9$	0.82

<sup>a</sup> All values are the average of three replicates  $\pm$  standard deviation.

M reveal that the larger the particle surface area, the better the chemical yields were. Yet, increasing the flow rate above 1.2 mL/min for the simultaneous separation of Pu along with Np was proven inappropriate, because the chemical yield ratio of  $^{237}\text{Np}/^{242}\text{Pu}$  deviated significantly from 1.0 when the flow rate was increased from 1.2 mL/min to 2.4 mL/min. Therefore, flow rates in the overall separation protocol were fixed to 1.2 mL/min throughout this work.

#### Valence Adjustment and Stability of Pu(IV) and Np(IV).

A pivotal step in the separation scheme is the adjustment of oxidation states of target radionuclides to Pu(IV) and Np(IV), for ensuring similar separation behavior of Pu and Np onto the anion exchanger. Our previous exploration and comparison of various methods for valence adjustment led us to conclude that the redox pair  $\text{K}_2\text{S}_2\text{O}_5$ –8 M  $\text{HNO}_3$  was the most effective agent.<sup>5</sup>

The same redox pair was employed in this work and the stability of Pu(IV) and Np(IV) after valence adjustment was investigated thereafter. Experimental results (see Table 3) demonstrate that Pu(IV) and Np(IV) might be stabilized in a 8 mol/L  $\text{HNO}_3$  milieu (sample solution) at room temperature for up to 24 h with acceptable chemical yields ( $>65\%$ ) for both Pu and Np and with satisfactory  $^{237}\text{Np}/^{242}\text{Pu}$  chemical yield ratios within the range of 0.93–1.05. The stabilization of Pu(IV) and Np(IV) in solution for  $\geq 5$  days at 3 °C with chemical yields of Pu and Np  $\geq 77\%$  and  $^{237}\text{Np}/^{242}\text{Pu}$  ratios from 0.96 to 1.00 is noteworthy.

**Separation Capability and Reusability of AG MP-1 M Resin.** To the best of our knowledge, no studies on the separation capability and reusability of AG MP-1 M anion exchanger have been reported so far for the processing of large-sized solid samples. Our analytical results (see Table 4) in the exploration of column separation capability showed that ca. 2 mL of AG MP-1 M resin can process a soil sample with a mass of up to 100 g with equally satisfactory chemical yields for Pu (85.2%) and Np (79.4%). However, undue back pressure was observed during sample loading when processing a 200-g soil sample. This suggests that

(25) Thompson, G. H.; Burney, G. A. *Processing of  $^{238}\text{Pu}$  and  $^{237}\text{Np}$  with macroporous anion exchange resin*, DP-1333 Chemical Separations Processes for Plutonium and Uranium, Report No. TID-4500-R61, UC-10, E. L. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, SC, 1973.

**Table 3. Variation of Chemical Yields of Pu and Np with the Time Interval between Valence Adjustment and Beginning of Column Separation**

Room Temperature				3 °C			
time (h)	Chemical Yield <sup>a</sup>			time (day)	Chemical Yield <sup>a</sup>		
	<sup>242</sup> Pu (%)	<sup>237</sup> Np (%)	ratio of <sup>237</sup> Np/ <sup>242</sup> Pu		<sup>242</sup> Pu (%)	<sup>237</sup> Np (%)	ratio of <sup>237</sup> Np/ <sup>242</sup> Pu
0	80.7	79.3	0.98	0	80.7	79.3	0.98
3.5	79.5	74.6	0.94	1	83.9	84.0	1.00
7.0	69.2	71.9	1.04	2	85.6	84.0	0.98
10.5	70.7	74.4	1.05	3	80.7	79.4	0.98
17.5	73.0	73.7	1.01	4	86.5	85.3	0.99
21.0	69.1	68.8	1.00	5	79.8	77.0	0.96
24.5	70.0	65.3	0.93				

<sup>a</sup> The uncertainties in the chemical yields of <sup>242</sup>Pu and <sup>237</sup>Np are all <10% (uncertainty is estimated considering the counting uncertainty in ICP-MS and sample, blank, tracer, and standard preparation).

**Table 4. Influence of Sample Size on the Analytical Performance of a ca. 2 mL Column Packed with AG MP-1M (100–200 Mesh) Resin for the Separation of Pu and Np from Soil Samples<sup>a</sup>**

sample size, g	Chemical Yield			Measured Value <sup>b</sup> (Bq/kg)	
	<sup>242</sup> Pu (%)	<sup>237</sup> Np (%)	ratio of <sup>237</sup> Np/ <sup>242</sup> Pu	<sup>239</sup> Pu	<sup>240</sup> Pu
10	87.8 ± 5.0	86.8 ± 6.0	0.99	0.14 ± 0.01	0.09 ± 0.01
20	84.8 ± 4.8	85.0 ± 5.6	1.00	0.14 ± 0.01	0.09 ± 0.01
50	75.2 ± 6.3	77.6 ± 7.2	1.03	0.14 ± 0.02	0.09 ± 0.01
100	85.2 ± 10.0	79.4 ± 9.5	0.93	0.14 ± 0.02	0.10 ± 0.01

<sup>a</sup> All values are the average of two replicates (± uncertainty). <sup>b</sup> The reference values of <sup>239</sup>Pu and <sup>240</sup>Pu concentrations in the Danish soil were reported to be 0.140 ± 0.008 and 0.098 ± 0.006 Bq/kg, respectively.

the small-sized AG MP-1 resin is not suitable for loading large amounts (>150 mL) of sample solution, as a consequence of resin shrinking in intimate contact with large volumes of highly concentrated nitric acid. Nevertheless, the volume of sample solution can be reduced through the improvement of the sample pretreatment procedure, for example, with the application of oxalate precipitation to remove most of the matrix elements and therefore minimize the size of the coprecipitate containing the target radionuclides.

Analytical results for evaluation of AG MP-1 M column reusability when handling 10 g of Danish soil spiked with different amounts of <sup>237</sup>Np are summarized in Table 5. Note that a ca. 2-mL column packed with AG MP-1 M resin could be reused up to 10 times with satisfactory chemical yields (>70%). Although it was still feasible to further reuse the column for three more assays, chemical yields started to decrease significantly and the interfering effects of uranium in the ICP-MS readouts became severe. Therefore, a 10-fold column reuse limitation is suggested to ensure accurate analysis. One should keep in mind that the on-column separation procedure might be completed within 3.5 h per sample, whereby 10 samples can be processed within 1.5 days using merely one chromatographic column. Accordingly, the SI system herein proposed and furnished with nine separation columns would be able to operate unattended for two weeks with a nominal workload of 90 samples when replacing SV2 and SV5 by an autosampler and fraction collector, respectively. In this case, the consumption of resin and analysis costs would be reduced to a large extent and the sample throughput improved significantly.

However, subtle deviations of measured <sup>237</sup>Np and Pu isotopes values from the expected concentrations were noted in some instances during the course of investigation of column reusability. This might be a consequence of the incomplete removal of Pu and Np from the anion exchanger, even with the usage of 60 mL of 0.05 mol/L H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> for column cleanup between samples. In further investigations of sample cross-contamination, a maximum analyte carryover of 5% for <sup>242</sup>Pu and 0.5% for <sup>237</sup>Np was detected in the consecutive processing of two Danish soil samples spiked with ca. 20 mBq of <sup>242</sup>Pu and ca. 2 mBq of <sup>237</sup>Np. Therefore, attention should be paid when reusing the AG MP-1 M resin for processing a variety of samples with different concentration levels of analytes, wherein stronger cleanup chemicals (e.g., hydrofluoric acid (HF) or ethylenediamine tetraacetic acid (EDTA)) might be needed to minimize carry-over effects.

**Method Validation.** Three certified reference materials, including two sediments (IAEA-385 and IAEA-135) and one seaweed (NIST-4359), and two reference materials from a laboratory round-robin intercomparison (namely, a Danish soil and an Irish Sea sediment) were analyzed by resorting to the proposed SI anion-exchange chromatographic method. Four aliquots of the reference samples were analyzed to test the trueness of the proposed method. This is determined under the criterion of the significant test score (*t*).<sup>26</sup> This parameter is calculated from the reference activity (*A*<sub>ref</sub>), the measured activity (*A*<sub>mea</sub>), the number of replicates (*n*), and the measured standard deviation (*s*<sub>mea</sub>), as follows:

$$t = \frac{|A_{\text{ref}} - A_{\text{mea}}| \sqrt{n}}{s_{\text{mea}}}$$

At the 0.05 significance level, the critical *t*-value (*t*<sub>crit</sub>) is 3.18 for *n* = 4. According to the *t*-test, all the *t*-values are below *t*<sub>crit</sub> (see Table 6); therefore, the overall experimental results are not significantly different from the reference or indicative values at the 95% probability level.

**Analytical Performance of the SI Anion-Exchange Chromatographic Manifold.** The SI manifold, using the AG MP-1 anion exchanger presented herein, is able to handle notably larger

(26) Miller, J. C.; Miller, J. N. *Statistics for Analytical Chemistry*, 3rd ed.; Ellis Horwood Limited: West Sussex, U.K., 1993.

**Table 5. Reusability of AG MP-1M (100–200 Mesh) Anion-Exchange Resin in a ca. 2 mL Column for the Separation of Pu and Np from Soil Samples<sup>a</sup>**

sequence number of sample	chemical yield of <sup>242</sup> Pu <sup>d</sup> (%)	Concentration of <sup>237</sup> Np <sup>b,d</sup> (Bq/kg)		Concentration of Pu Isotopes <sup>c,d</sup> (Bq/kg)	
		measured	expected	<sup>239</sup> Pu	<sup>240</sup> Pu
1	83.5	0.30	0.29	0.14	0.11
2	96.0	0.16	0.18	0.15	0.10
3	91.0	0.07	0.08	0.12	0.12
4	83.6	0.04	0.04	0.15	0.12
5	90.2	0.16	0.19	0.15	0.10
6	87.8	0.16	0.13	0.14	0.12
7	81.1	0.07	0.07	0.15	0.12
8	86.4	0.04	0.04	0.15	0.12
9	79.1	0.25	0.28	0.15	0.13
10	70.6	<DL <sup>e</sup>	0.00	0.15	0.10
11	63.8	0.04	0.05	0.14	0.11
12	66.0	0.13	0.12	0.15	0.11
13	62.0	<DL	0.00	0.14	0.12

<sup>a</sup> Sixty milliliters (60 mL) of 0.05 mol/L H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> was used for column cleanup between samples. <sup>b</sup> Different amounts of <sup>237</sup>Np were used to enrich the Danish soil, inducing different concentrations of <sup>237</sup>Np in the samples (the original <sup>237</sup>Np concentration in the soil is below the detection limit (DL)). <sup>c</sup> The reference values of <sup>239</sup>Pu and <sup>240</sup>Pu concentrations in the Danish soil were reported to be 0.140 ± 0.008 and 0.098 ± 0.006 Bq/kg, respectively. <sup>d</sup> The uncertainties in chemical yields of <sup>242</sup>Pu and activity concentrations of <sup>237</sup>Np and <sup>239</sup>Pu are all <10%. <sup>e</sup> The detection limit (DL) of <sup>237</sup>Np is 1.5 pg/L (or 15 fg in 10 mL of eluate, corresponding to 0.00039 mBq of <sup>237</sup>Np).

**Table 6. Analytical Results of Environmental Solids by Resorting to the Proposed SI Anion-Exchange Method<sup>a</sup>**

sample	IAEA-135 sediment	Irish Sea sediment	IAEA-385 sediment	Danish soil	NIST-4359 seaweed <sup>c</sup>
weight (g)	0.5	0.5	1.0	10.0	20.0
chemical yield (%)	72.1 ± 4.2	69.0 ± 5.1	74.4 ± 4.2	88.9 ± 4.7	68.4 ± 3.3
measured value <sup>b</sup> (Bq/kg)					
<sup>237</sup> Np	0.91 ± 0.06 [1.85]	0.99 ± 0.05 [0.10]	0.023 ± 0.006 [1.27]	0.103 ± 0.002 [1.73]	0.00020 ± 0.00006 [0.75]
<sup>239</sup> Pu	127 ± 5 [1.39]	230 ± 7 [1.73]	1.7 ± 0.2 [1.91]	0.148 ± 0.009 [1.54]	0.081 ± 0.002 [2.60]
<sup>240</sup> Pu	97 ± 3 [1.85]	173 ± 2 [1.73]	1.1 ± 0.1 [1.39]	0.100 ± 0.008 [0.43]	0.055 ± 0.006 [0.58]
<sup>239</sup> + <sup>240</sup> Pu	224 ± 7 [2.72]	403 ± 9 [3.08]	2.8 ± 0.2 [1.56]	0.25 ± 0.02 [1.04]	0.136 ± 0.008 [0.14]
expected value <sup>d</sup> (Bq/kg)					
<sup>237</sup> Np	0.846 ± 0.045 <sup>b</sup> (ref 7)	0.987 ± 0.048 <sup>b</sup> (ref 7)	0.0186 ± 0.0038 <sup>b</sup> (ref 28)	0.101 ± 0.002 <sup>i</sup>	0.000173 (0.000152–0.000198) <sup>g</sup>
<sup>239</sup> Pu	123.0 ± 3.8 <sup>b</sup> (ref 7)	237.0 ± 5.0 <sup>b</sup> (ref 7)	1.92 (1.30–2.07) <sup>g</sup>	0.140 ± 0.008 <sup>b</sup> (ref 23)	0.0840 ± 0.0033 <sup>e</sup>
<sup>240</sup> Pu	93.8 ± 2.3 <sup>b</sup> (ref 7)	171.0 ± 4.9 <sup>b</sup> (ref 7)	1.18 (0.97–1.32) <sup>g</sup>	0.098 ± 0.006 <sup>b</sup> (ref 23)	0.057 (0.049–0.066) <sup>g</sup>
<sup>239</sup> + <sup>240</sup> Pu	213 (205–226) <sup>f</sup>	419.0 ± 10.6 <sup>b</sup> (ref 7)	2.98 (2.81–3.13) <sup>f</sup>	0.238 ± 0.014 <sup>b</sup> (ref 23)	0.1296 ± 0.0075 <sup>e</sup>

<sup>a</sup> All values are the average of four replicates (±standard deviation). <sup>b</sup> Numbers in brackets are  $|t|_{\text{exp}}$  values at the 95% probability level. The critical  $t$ -value ( $t_{\text{crit}}$ ) is 3.18 for  $n = 4$ . <sup>c</sup> The information value of <sup>237</sup>Np in the certification of NIST-4359 seaweed was provided by Risø-DTU; however, the units for <sup>237</sup>Np activity were presented incorrectly in the certification datasheet. The correct value should be 0.17 mBq/kg, with a range of 0.152–0.198 mBq/kg. <sup>d</sup> Expected values include the certified value, the recommended value, the information value, the literature value, and that added to the sample. <sup>e</sup> Includes only the certified value. <sup>f</sup> Includes only the recommended value. <sup>g</sup> Includes only the information value. <sup>h</sup> Includes only the literature value. <sup>i</sup> Includes only that added to the sample.

amounts of solid samples (up to 100 g of soil), in comparison with almost all the previously published works for the simultaneous determination of Pu isotopes and <sup>237</sup>Np wherein ≤10 g of soil were processed,<sup>7,9,10,17,27</sup> and, therefore, sample enrichment factors might be improved by a factor of 10 or better. Compared with previous publications devoted to either nuclear fuel<sup>8,27</sup> or highly contaminated environmental samples,<sup>10</sup> the developed method is more suitable for determination of ultratrace levels of <sup>239</sup>Pu, <sup>240</sup>Pu, and <sup>237</sup>Np, as a result of the low ICP-MS detection limits of <sup>239</sup>Pu, <sup>240</sup>Pu, and <sup>237</sup>Np (viz., 1.5 pg/L) and the likelihood of handling large-sized samples. Chemical yields, especially for <sup>237</sup>Np (85 ± 6.0%), are significantly improved, compared to those of former reports.<sup>5,6,9</sup>

The automated processing of samples in a programmable SI sequence leads to not only expeditious assays of Pu and Np

(different steps in the analytical procedure can be executed concurrently), compared with the conventional batch-wise method using large-sized anion-exchange columns,<sup>7</sup> but also to simplicity, reliability, a decrease in uncertainty measurements (because of minimal human intervention), and improved safety of the analyst as well. Last but not least, enhanced repeatability is obtained, as a consequence of the precise control of sample and reagent volumes and flow rates within the SI network. The reuse of separation columns following appropriate washing sequences gives rise to cost-effective approaches. In addition, the SI system might be reconfigured at will for the simultaneous processing of several samples via multicolumn designs.

## CONCLUSION

A sequential injection (SI)-based anion-exchange chromatographic method is proposed herein for the automated and simultaneous determination of <sup>239</sup>Pu, <sup>240</sup>Pu, and <sup>237</sup>Np in environmental solids, using a macroporous anion exchanger (AG MP-1 M). Our analytical results demonstrate that (i) <sup>242</sup>Pu performs well as a chemical yield tracer for <sup>237</sup>Np because

(27) Perna, L.; Bocci, F.; de las Heras, L. A.; De Pablo, J.; Betti, M. *J. Anal. Spectrom.* **2002**, *17*, 1166–1171.

(28) Pham, M. K.; Sanchez-Cabeza, J. A.; Povinec, P. P. *Report on the worldwide intercomparison exercise IAEA-385 Radionuclides in Irish Sea sediment*, Report No. IAEA/AL/151 IAEA/MEL/7, International Atomic Energy Agency, Monaco, 2005; pp 12–13.



excellent agreement between chemical yields of  $^{242}\text{Pu}$  and  $^{237}\text{Np}$  is obtained throughout this work; (ii) a small sized column packed with ca. 2 mL of AG MP-1 M resin suffices to process up to 100 g of soil; (iii) the separation column can be reused up to 10-fold with no appreciable deterioration of chemical yields; and (iv) the automated method simplifies the analytical workloads, compared to error-prone batch-wise methods.

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